



US009478758B1

(12) **United States Patent**  
**Tsai**

(10) **Patent No.:** **US 9,478,758 B1**  
(45) **Date of Patent:** **Oct. 25, 2016**

(54) **ORGANIC ELECTROLUMINESCENT MATERIALS AND DEVICES**

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(\*) Notice: Subject to any disclaimer, the term of this  
patent is extended or adjusted under 35  
U.S.C. 154(b) by 0 days.

(21) Appl. No.: **14/707,622**

(22) Filed: **May 8, 2015**

(51) **Int. Cl.**  
**H01L 51/00** (2006.01)  
**C07F 15/00** (2006.01)  
**C09K 11/02** (2006.01)  
**C09K 11/06** (2006.01)  
**H01L 51/50** (2006.01)

(52) **U.S. Cl.**  
CPC ..... **H01L 51/0088** (2013.01); **C07F 15/002**  
(2013.01); **C09K 11/025** (2013.01); **C09K**  
**11/06** (2013.01); **H01L 51/0074** (2013.01);  
**H01L 51/0085** (2013.01); **C09K 2211/185**  
(2013.01); **H01L 51/5016** (2013.01); **H01L**  
**51/5056** (2013.01); **H01L 51/5072** (2013.01);  
**H01L 51/5088** (2013.01); **H01L 51/5092**  
(2013.01); **H01L 51/5096** (2013.01)

(58) **Field of Classification Search**  
CPC ..... H01L 2251/308; H01L 51/0054;  
H01L 51/5072  
See application file for complete search history.

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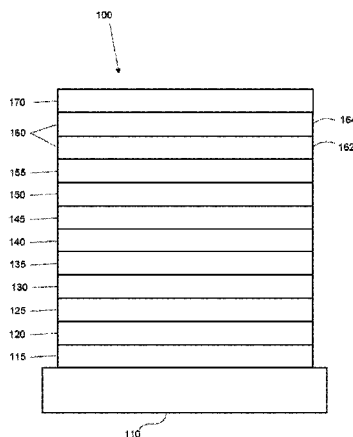
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(57) **ABSTRACT**

Organic materials comprising pendant redox-active metal-  
locence groups are described. The hole transport property of  
these systems can be modulated through the metallocence  
moiety.

**15 Claims, 2 Drawing Sheets**



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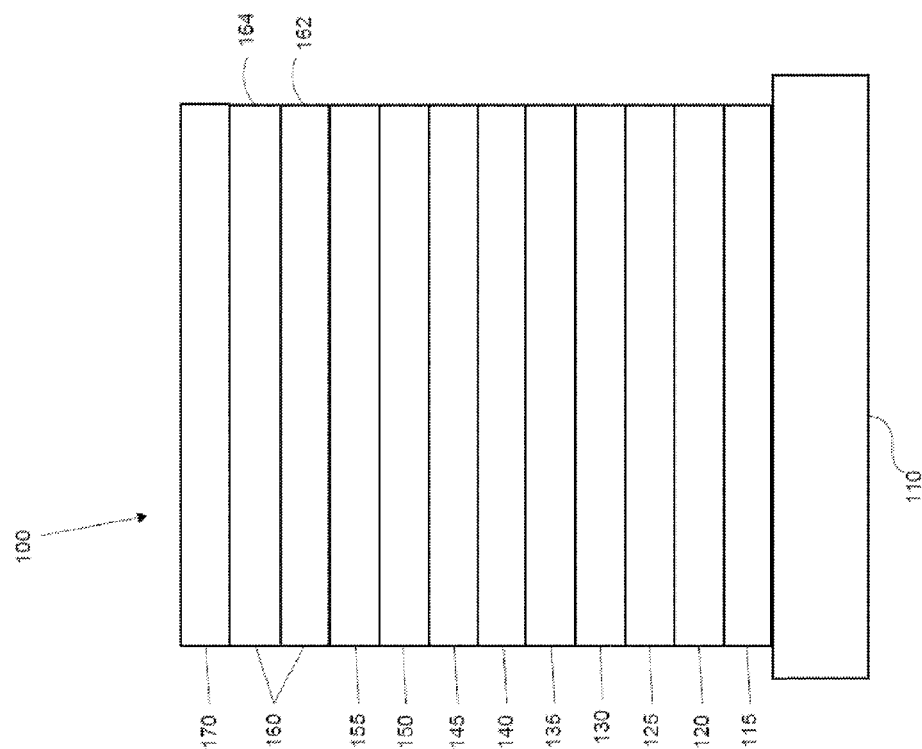


Figure 1

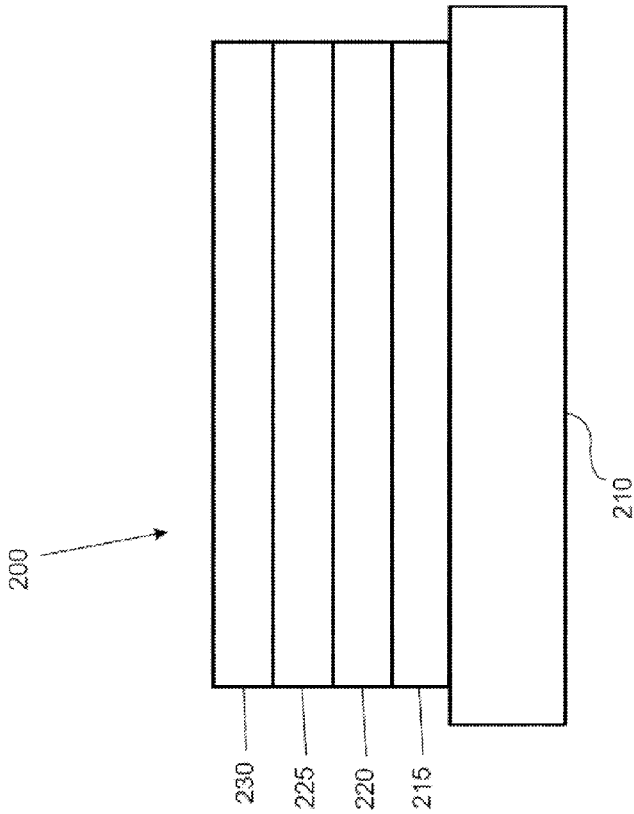


Figure 2

1

# ORGANIC ELECTROLUMINESCENT MATERIALS AND DEVICES

## PARTIES TO A JOINT RESEARCH AGREEMENT

The claimed invention was made by, on behalf of, and/or in connection with one or more of the following parties to a joint university corporation research agreement: Regents of the University of Michigan, Princeton University, University of Southern California, and the Universal Display Corporation. The agreement was in effect on and before the date the claimed invention was made, and the claimed invention was made as a result of activities undertaken within the scope of the agreement.

## FIELD OF THE INVENTION

The present invention relates to novel metallocenes useful for charge transport and devices, such as organic light emitting diodes, including the same.

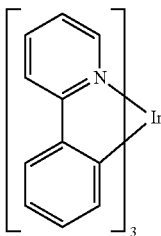
## BACKGROUND

Opto-electronic devices that make use of organic materials are becoming increasingly desirable for a number of reasons. Many of the materials used to make such devices are relatively inexpensive, so organic opto-electronic devices have the potential for cost advantages over inorganic devices. In addition, the inherent properties of organic materials, such as their flexibility, may make them well suited for particular applications such as fabrication on a flexible substrate. Examples of organic opto-electronic devices include organic light emitting devices (OLEDs), organic phototransistors, organic photovoltaic cells, and organic photodetectors. For OLEDs, the organic materials may have performance advantages over conventional materials. For example, the wavelength at which an organic emissive layer emits light may generally be readily tuned with appropriate dopants.

OLEDs make use of thin organic films that emit light when voltage is applied across the device. OLEDs are becoming an increasingly interesting technology for use in applications such as flat panel displays, illumination, and backlighting. Several OLED materials and configurations are described in U.S. Pat. Nos. 5,844,363, 6,303,238, and 5,707,745, which are incorporated herein by reference in their entirety.

One application for phosphorescent emissive molecules is a full color display. Industry standards for such a display call for pixels adapted to emit particular colors, referred to as "saturated" colors. In particular, these standards call for saturated red, green, and blue pixels. Color may be measured using CIE coordinates, which are well known to the art.

One example of a green emissive molecule is tris(2-phenylpyridine) iridium, denoted Ir(ppy)<sub>3</sub>, which has the following structure:



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In this, and later figures herein, we depict the dative bond from nitrogen to metal (here, Ir) as a straight line.

As used herein, the term "organic" includes polymeric materials as well as small molecule organic materials that may be used to fabricate organic opto-electronic devices. "Small molecule" refers to any organic material that is not a polymer, and "small molecules" may actually be quite large. Small molecules may include repeat units in some circumstances. For example, using a long chain alkyl group as a substituent does not remove a molecule from the "small molecule" class. Small molecules may also be incorporated into polymers, for example as a pendent group on a polymer backbone or as a part of the backbone. Small molecules may also serve as the core moiety of a dendrimer, which consists of a series of chemical shells built on the core moiety. The core moiety of a dendrimer may be a fluorescent or phosphorescent small molecule emitter. A dendrimer may be a "small molecule," and it is believed that all dendrimers currently used in the field of OLEDs are small molecules.

As used herein, "top" means furthest away from the substrate, while "bottom" means closest to the substrate. Where a first layer is described as "disposed over" a second layer, the first layer is disposed further away from substrate. There may be other layers between the first and second layer, unless it is specified that the first layer is "in contact with" the second layer. For example, a cathode may be described as "disposed over" an anode, even though there are various organic layers in between.

As used herein, "solution processible" means capable of being dissolved, dispersed, or transported in and/or deposited from a liquid medium, either in solution or suspension form.

A ligand may be referred to as "photoactive" when it is believed that the ligand directly contributes to the photoactive properties of an emissive material. A ligand may be referred to as "ancillary" when it is believed that the ligand does not contribute to the photoactive properties of an emissive material, although an ancillary ligand may alter the properties of a photoactive ligand.

As used herein, and as would be generally understood by one skilled in the art, a first "Highest Occupied Molecular Orbital" (HOMO) or "Lowest Unoccupied Molecular Orbital" (LUMO) energy level is "greater than" or "higher than" a second HOMO or LUMO energy level if the first energy level is closer to the vacuum energy level. Since ionization potentials (IP) are measured as a negative energy relative to a vacuum level, a higher HOMO energy level corresponds to an IP having a smaller absolute value (an IP that is less negative). Similarly, a higher LUMO energy level corresponds to an electron affinity (EA) having a smaller absolute value (an EA that is less negative). On a conventional energy level diagram, with the vacuum level at the top, the LUMO energy level of a material is higher than the HOMO energy level of the same material. A "higher" HOMO or LUMO energy level appears closer to the top of such a diagram than a "lower" HOMO or LUMO energy level.

As used herein, and as would be generally understood by one skilled in the art, a first work function is "greater than" or "higher than" a second work function if the first work function has a higher absolute value. Because work functions are generally measured as negative numbers relative to vacuum level, this means that a "higher" work function is more negative. On a conventional energy level diagram, with the vacuum level at the top, a "higher" work function is illustrated as further away from the vacuum level in the

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downward direction. Thus, the definitions of HOMO and LUMO energy levels follow a different convention than work functions.

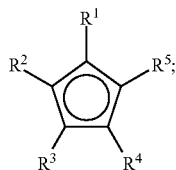
More details on OLEDs, and the definitions described above, can be found in U.S. Pat. No. 7,279,704, which is incorporated herein by reference in its entirety.

To achieve efficient OLEDs, a balance charge carrier transport and a broad recombination zone are required. This task can be accomplished by the design of bipolar host materials. In bipolar host materials, holes and electrons are transported through different parts of the molecule. The hole transport in many cases occurs through carbazole units, whereas electron transport is often realized by the use of electron accepting N-heterocycles such as triazines or oxadiazoles. There is a need in the art for novel compounds that can improve OLED device performance parameters. The present invention addresses this unmet need.

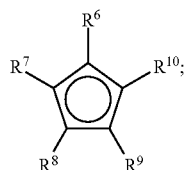
### SUMMARY OF THE INVENTION

According to an embodiment, a compound is provided comprising an osmocene structure having a formula of  $\text{Os}(\text{L}^1)(\text{L}^2)$ ;

wherein  $\text{L}^1$  has the formula:



wherein  $\text{L}^2$  has the formula:



wherein  $\text{R}^1$  to  $\text{R}^{10}$  are each independently selected from the group consisting of hydrogen, deuterium, halogen, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, heterocyclyl, acyl, carbonyl, carboxylic acid, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof; and

wherein at least one of  $\text{R}^1$  to  $\text{R}^{10}$  comprises an aryl group or a heteroaryl group.

In one embodiment at least one of  $\text{R}^1$  to  $\text{R}^{10}$  comprises an aryl group having at least 12 carbon atoms or a heteroaryl group having at least 4 carbon atoms.

In another embodiment, at least one of  $\text{R}^1$  to  $\text{R}^{10}$  comprises at least one chemical group selected from the group consisting of triphenylene, carbazole, dibenzothiophene, dibenzofuran, dibenzoselenophene, azatriphenylene, azacarbazole, aza-dibenzothiophene, aza-dibenzofuran, and aza-dibenzoselenophene. In another embodiment, at least one of  $\text{R}^1$  to  $\text{R}^{10}$  comprises at least one chemical group selected from the group consisting of biphenyl, triphenyl, triphenylene, naphthalene, anthracene, phenalene, phenanthrene, fluorene, pyrene, chrysene, perylene, and azulene. In another

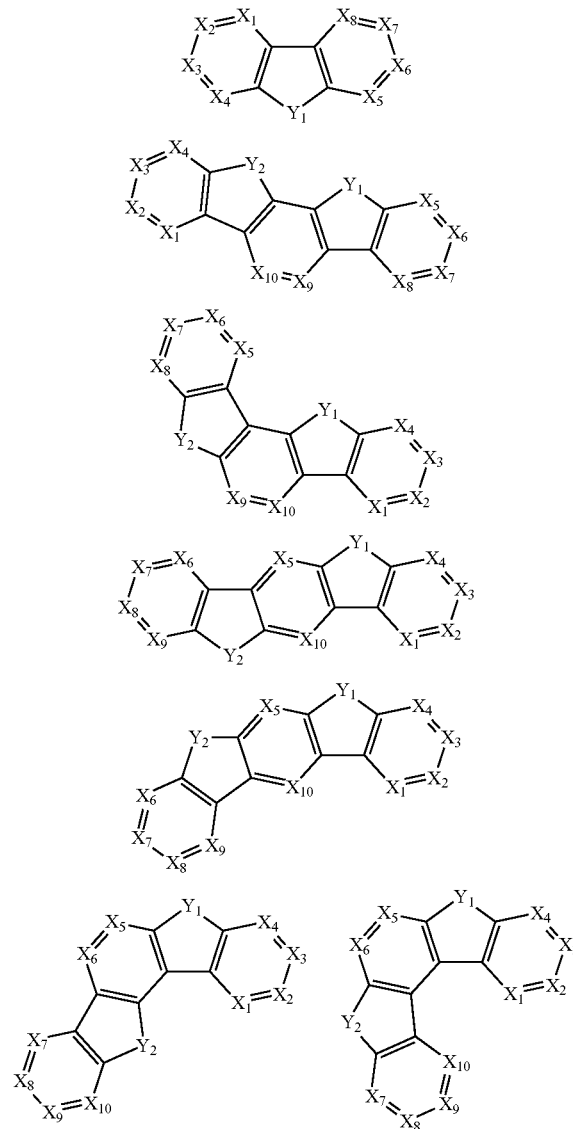
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embodiment, at least one of  $\text{R}^1$  to  $\text{R}^{10}$  comprises at least one chemical group selected from the group consisting of dibenzothiophene, dibenzofuran, dibenzoselenophene, furan, thiophene, benzofuran, benzothiophene, benzoselenophene, carbazole, indolocarbazole, pyridylindole, pyrrolodipyrindine, pyrazole, imidazole, triazole, oxazole, thiazole, oxadiazole, oxatriazole, dioxazole, thiadiazole, pyridine, pyridazine, pyrimidine, pyrazine, triazine, oxazine, oxathiazine, oxadiazine, indole, benzimidazole, indazole, indoxazine, benzoxazole, benzisoxazole, benzothiazole, quinoxaline, isoquinoline, cinnoline, quinazoline, quinoxaline, naphthyridine, phthalazine, pteridine, xanthene, acridine, phenazine, phenothiazine, phenoxazine, benzofurofuran, furodipyrindine, benzothienopyridine, thienodipyrindine, benzoselenophenopyridine, selenophenodipyrindine, aza analogs thereof, and combinations thereof.

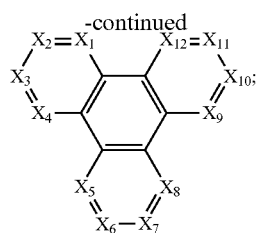
In one embodiment, at least one of  $\text{R}^1$  to  $\text{R}^{10}$  is L-G;

wherein L is a direct bond or an organic linker; and

wherein G is selected from the group consisting of:





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wherein  $Y_1$  and  $Y_2$  are independently selected from the group consisting of  $NR^{11}$ ,  $CR^{11}R^{12}$ , O, S, and Se;

wherein  $X_1$  to  $X_{12}$  are independently selected from the group consisting of  $CR^{13}$  and N, and

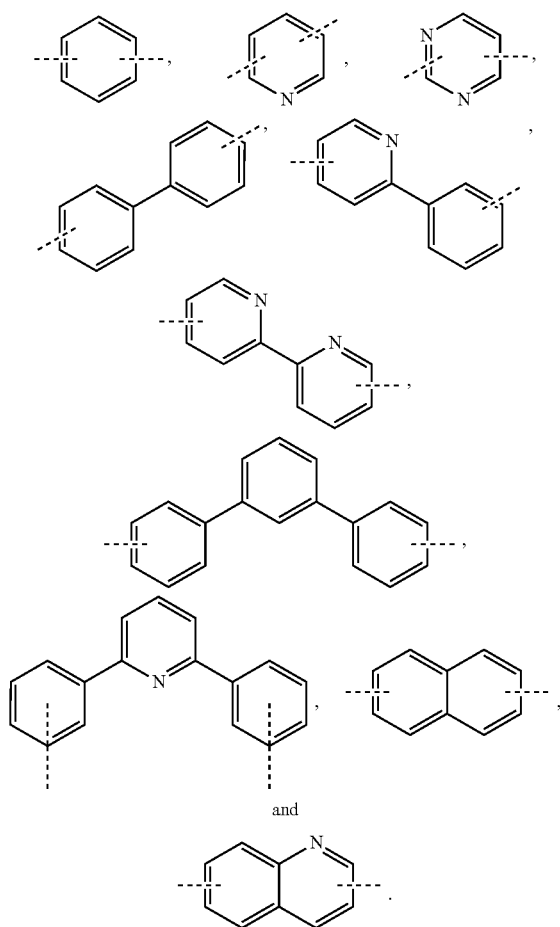
wherein  $R^{11}$ ,  $R^{12}$ , and  $R^{13}$  are each independently selected from the group consisting of hydrogen, deuterium, halogen, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acid, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof; and

wherein any two adjacent substituents of  $R^{11}$ ,  $R^{12}$ , and  $R^{13}$  are optionally fused or joined to form a ring.

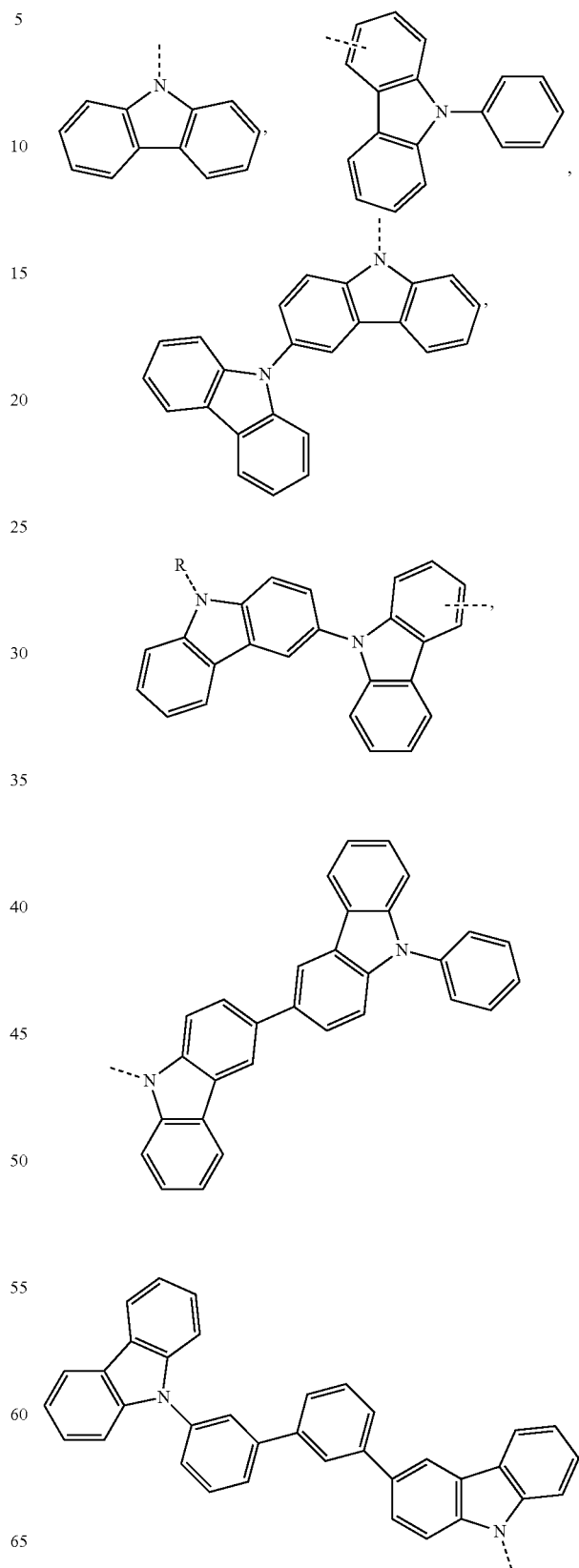
In one embodiment, at least one of  $R^1$  to  $R^{10}$  comprises at least one carbazole group.

In one embodiment, L is selected from the group consisting of:

Direct bond,

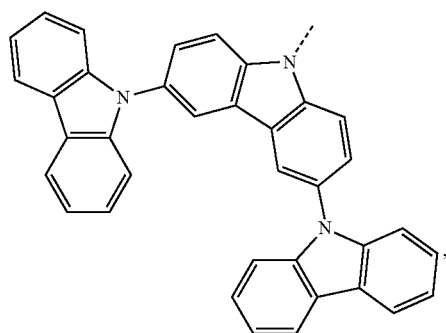
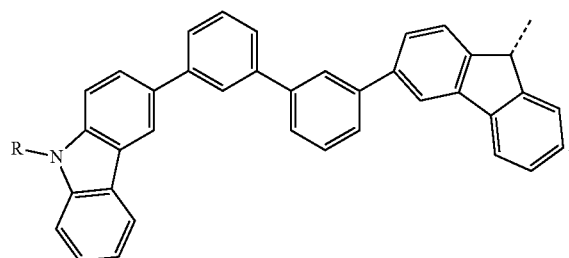
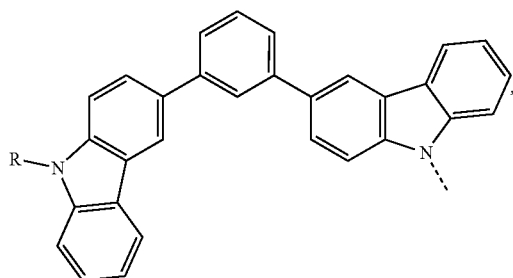
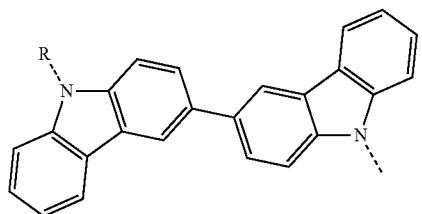
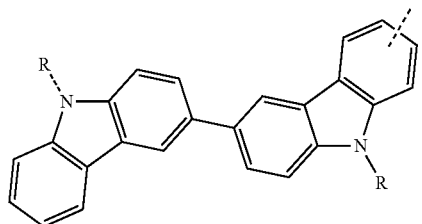
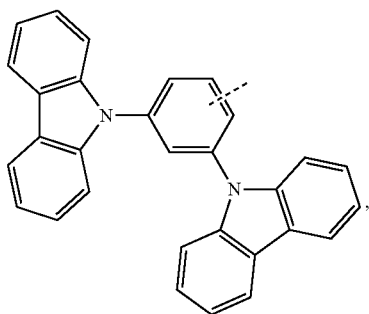
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In one embodiment, G is selected from the group consisting of:



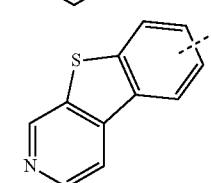
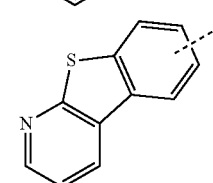
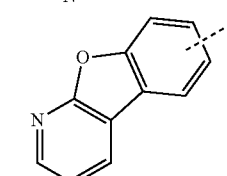
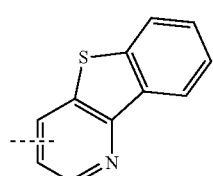
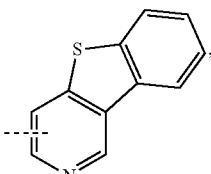
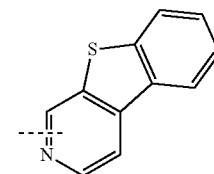
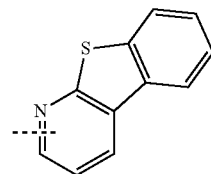
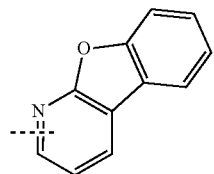
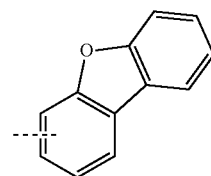
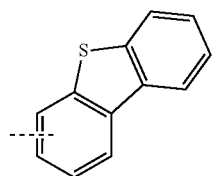
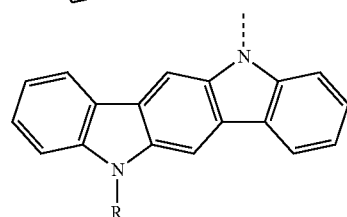
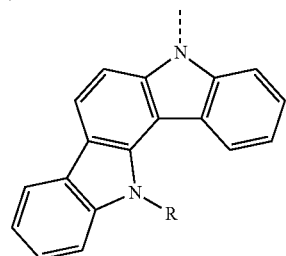
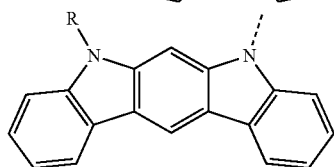
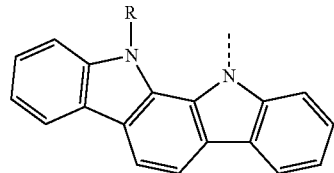
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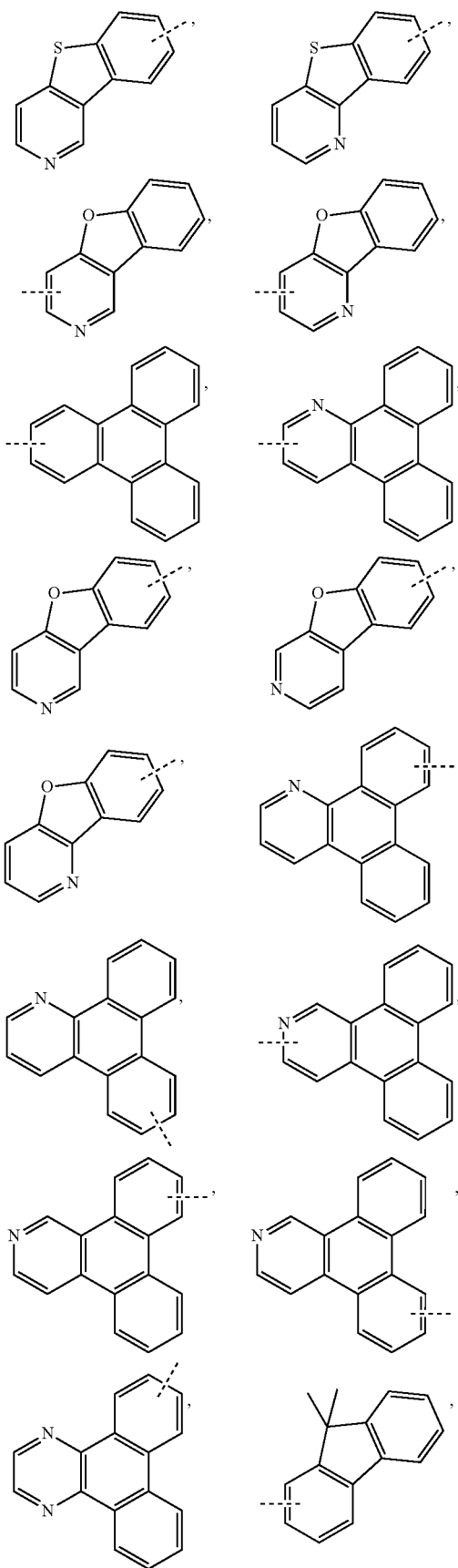
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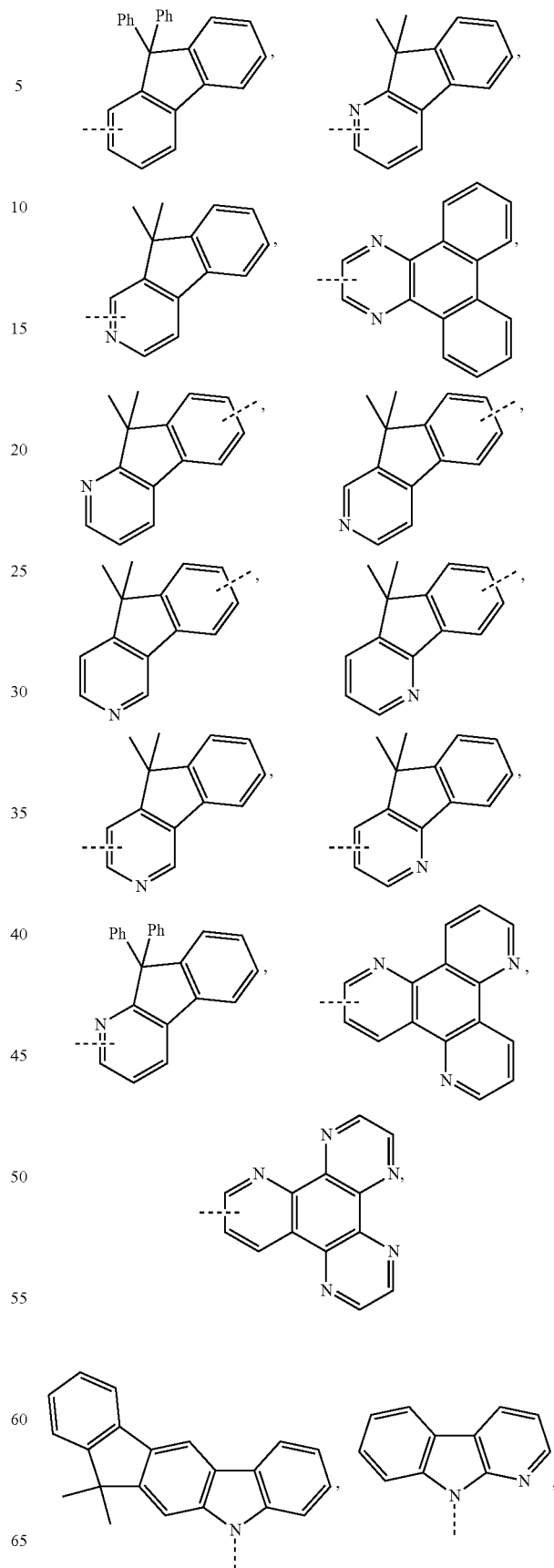
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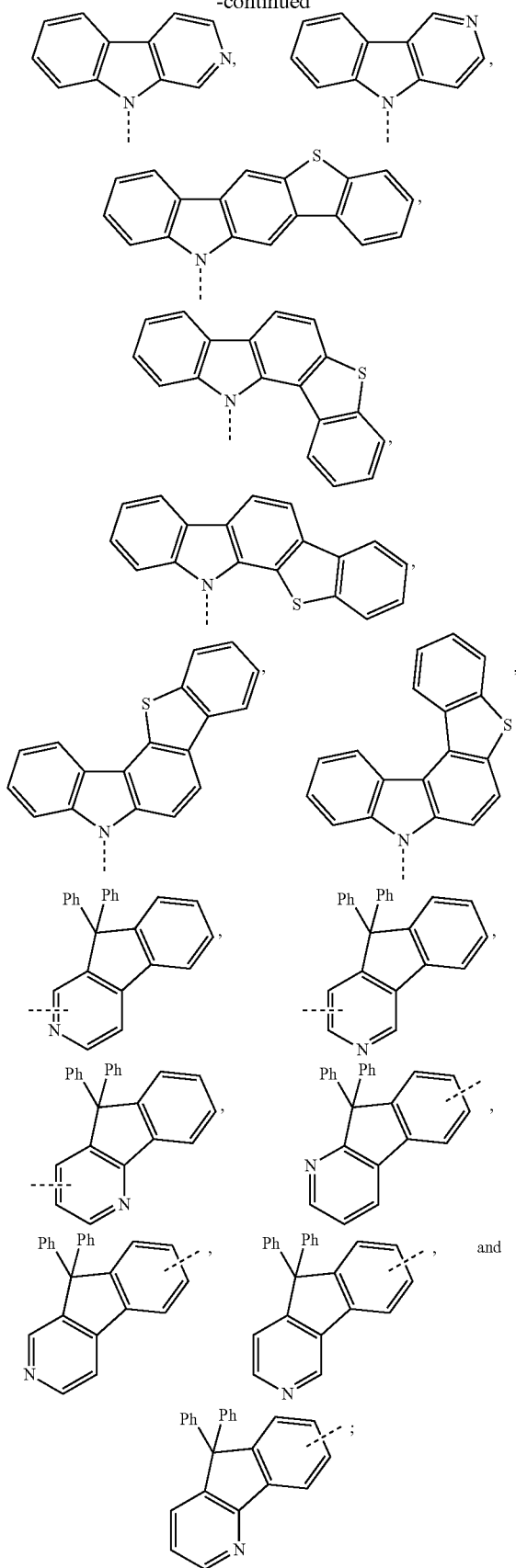
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wherein R is selected from the group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, aryl-alkyl, alkoxy, aryl, heteroaryl, aryloxy, amino, and combinations thereof.

In one embodiment the compound is selected from the group consisting of:

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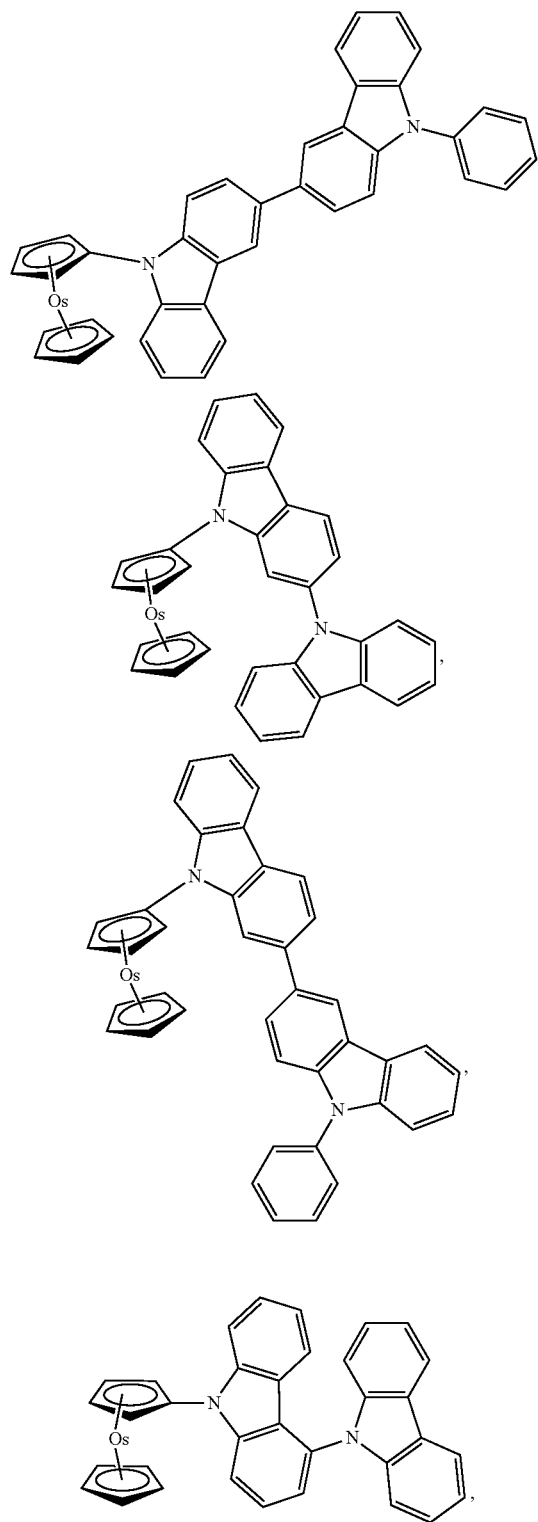
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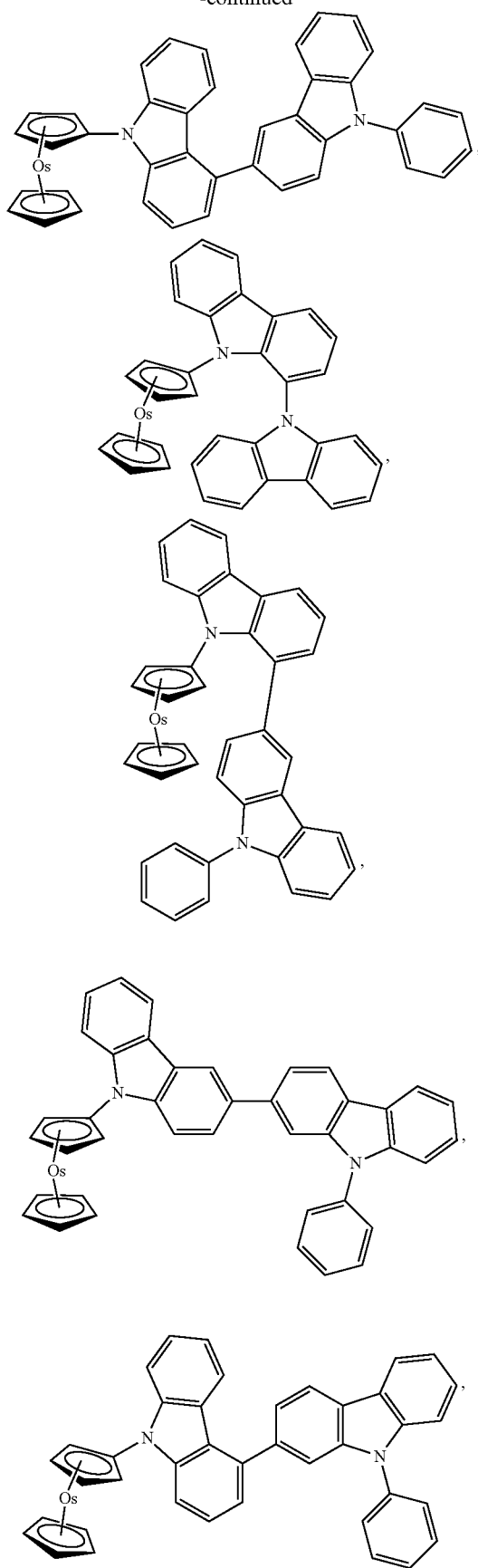
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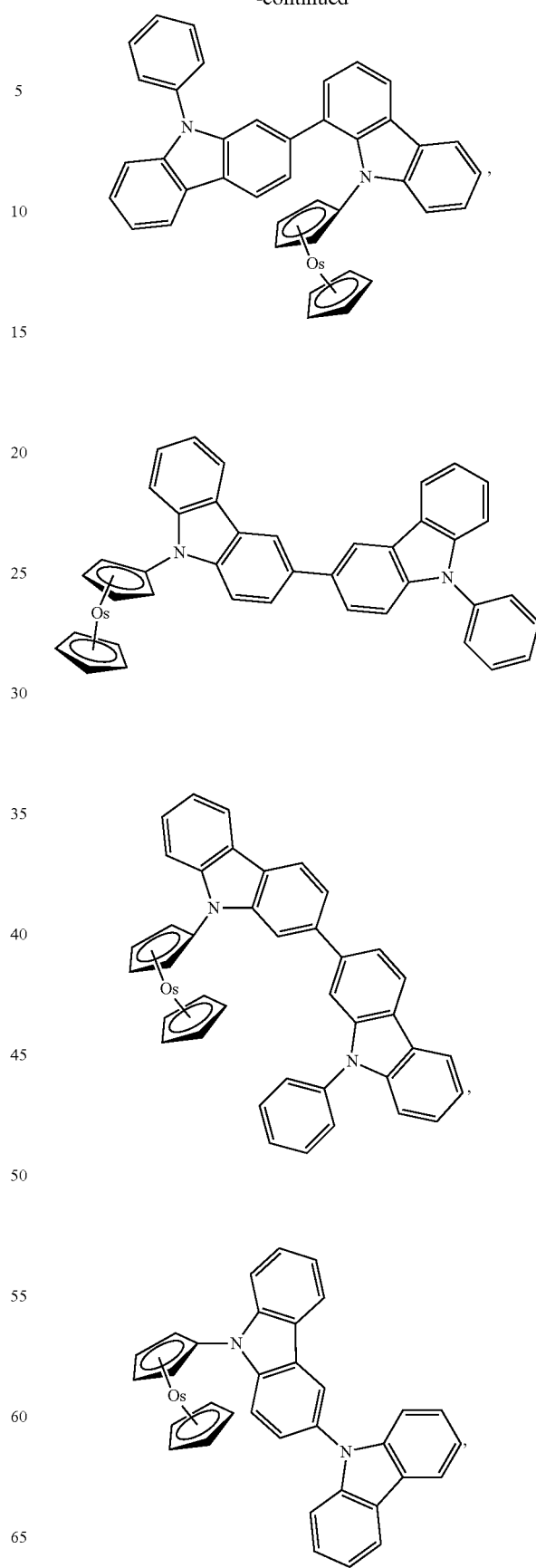


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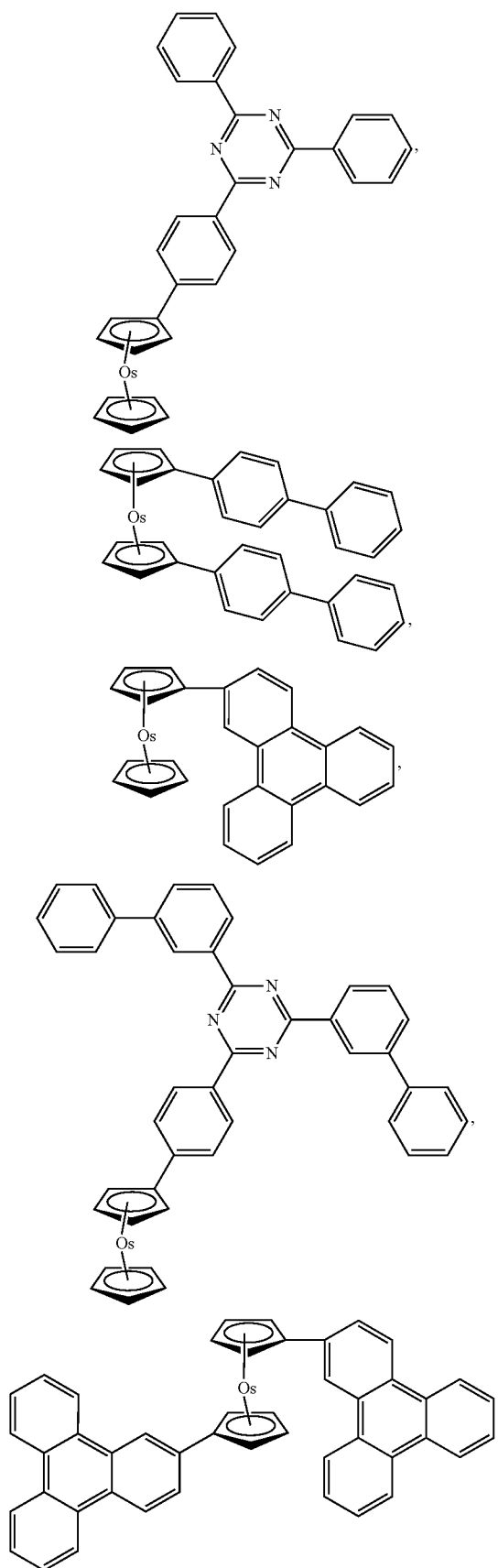
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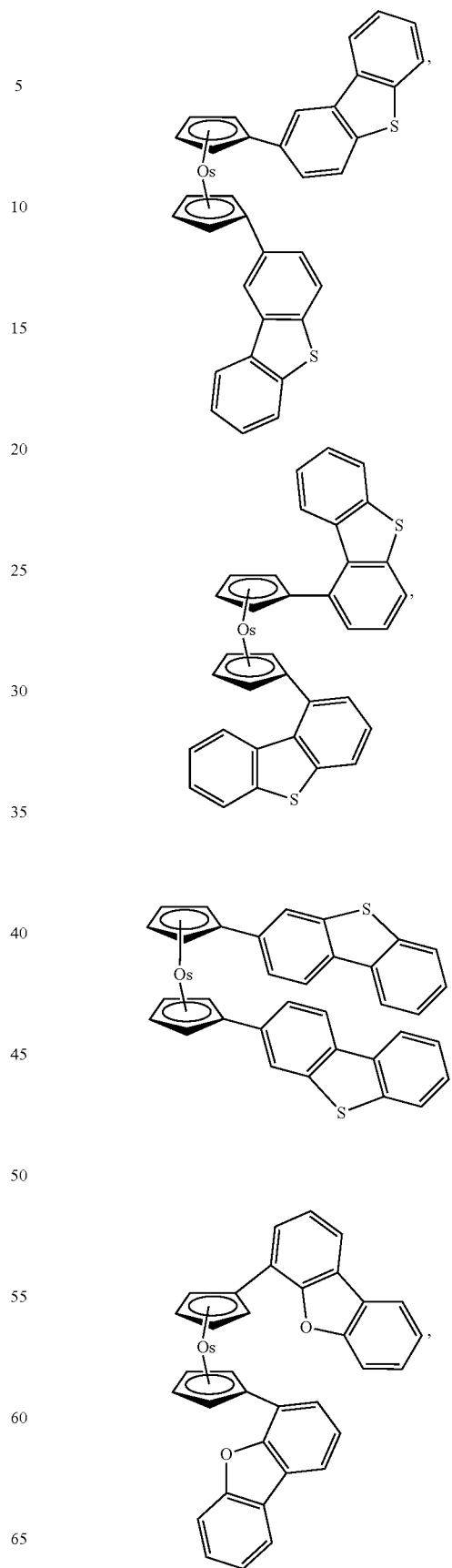


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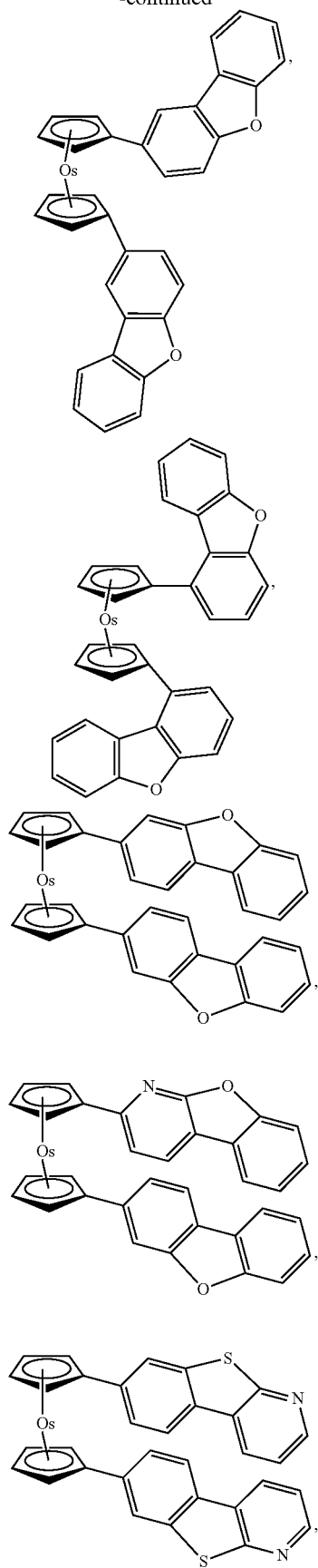
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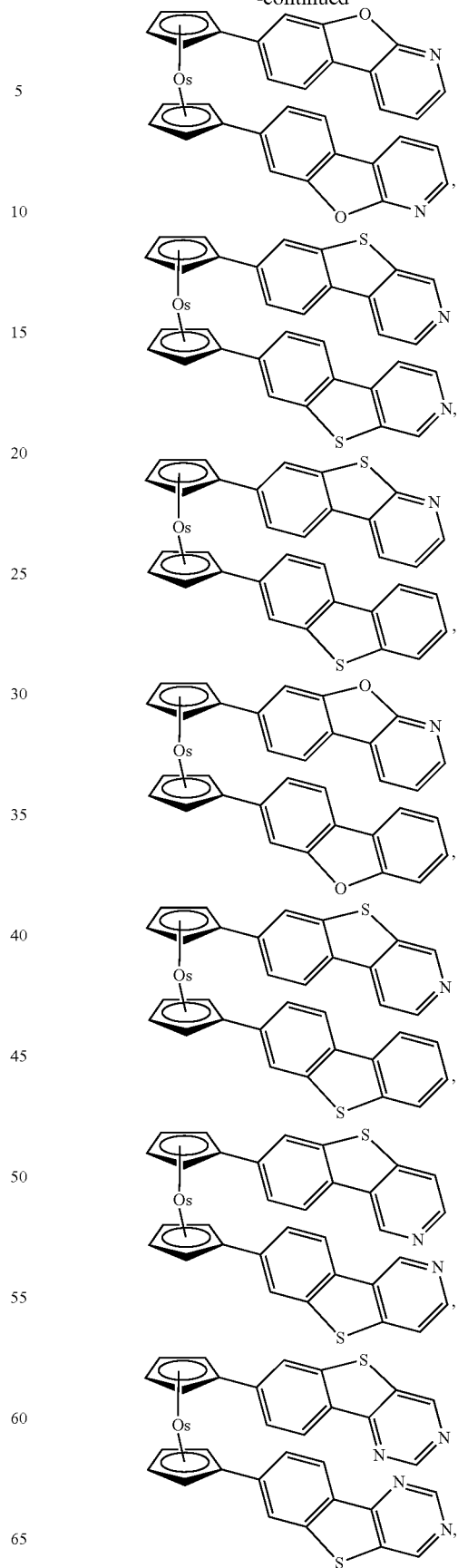


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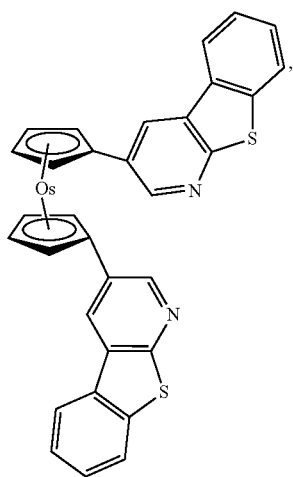
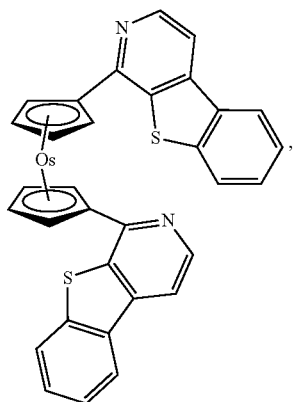
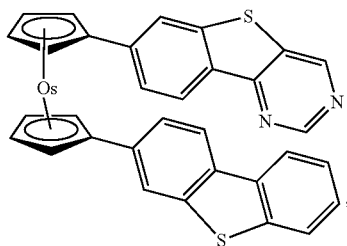
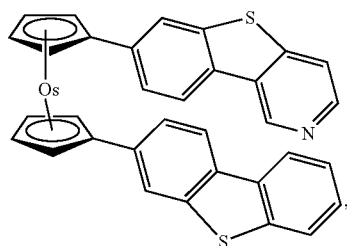
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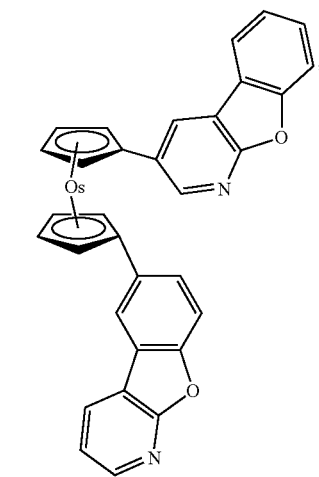
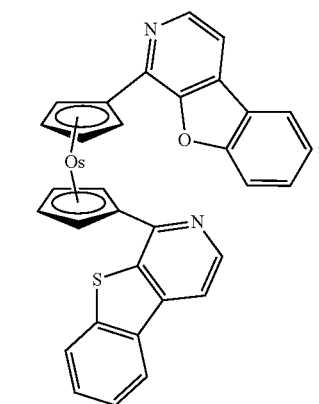
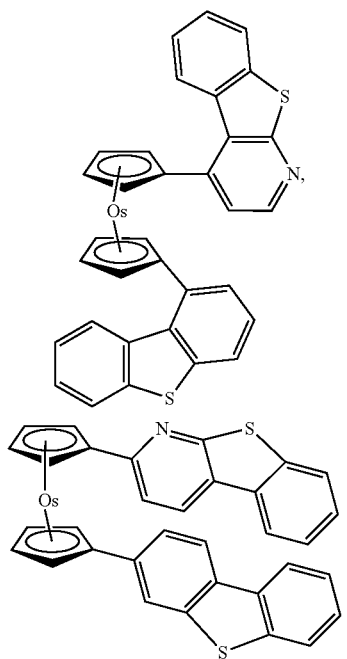
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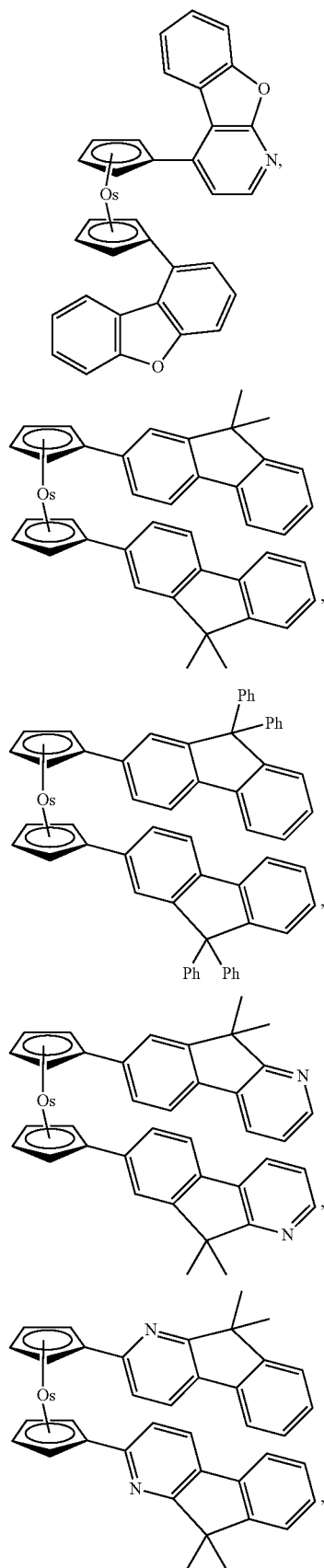
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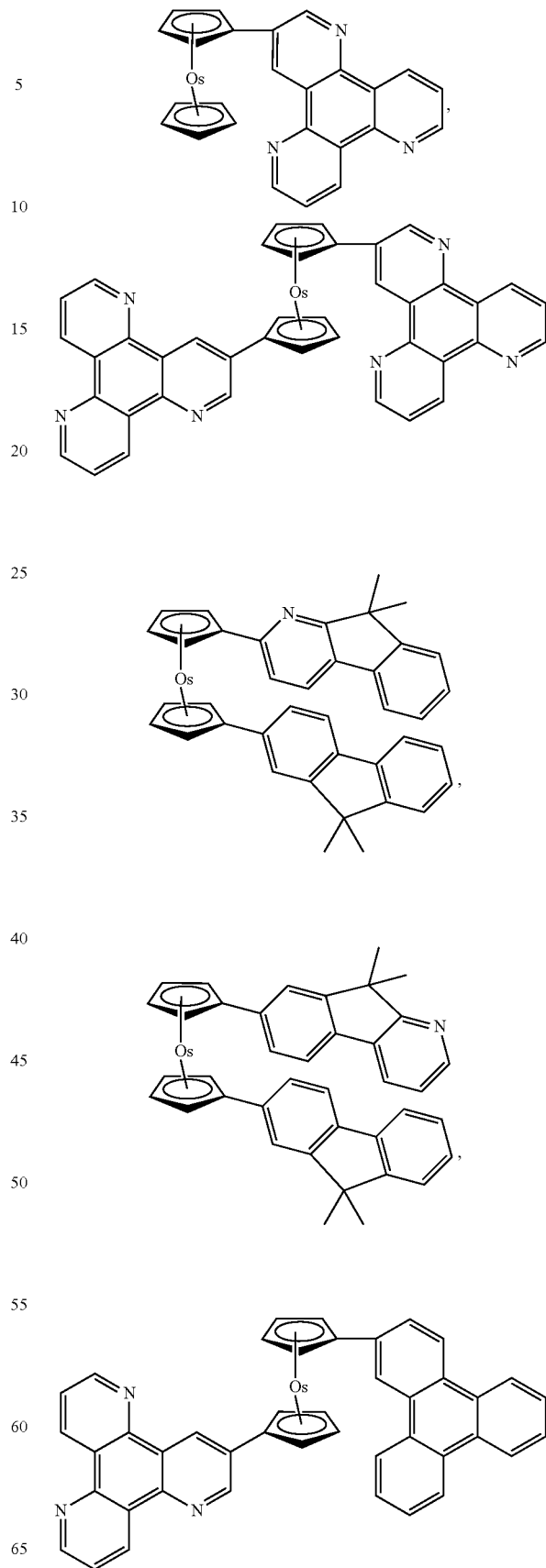


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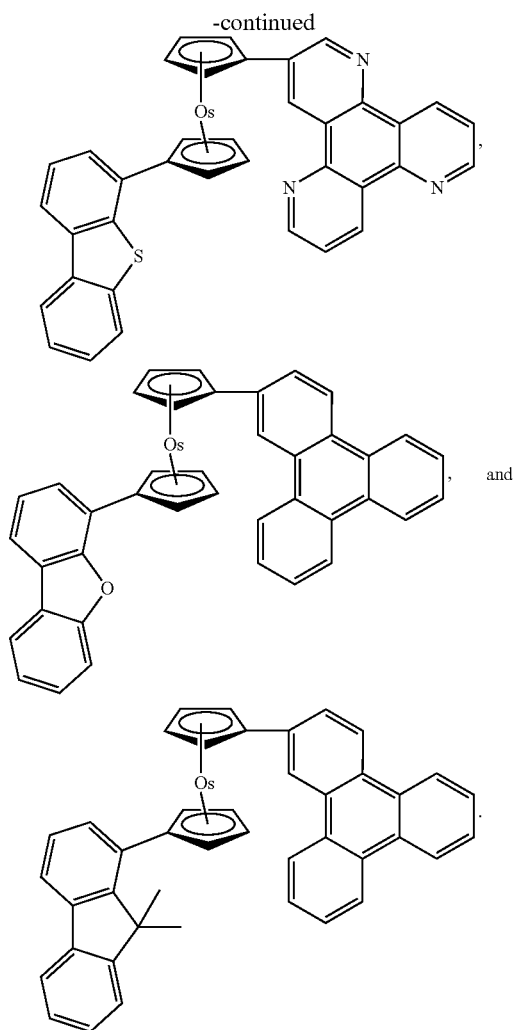
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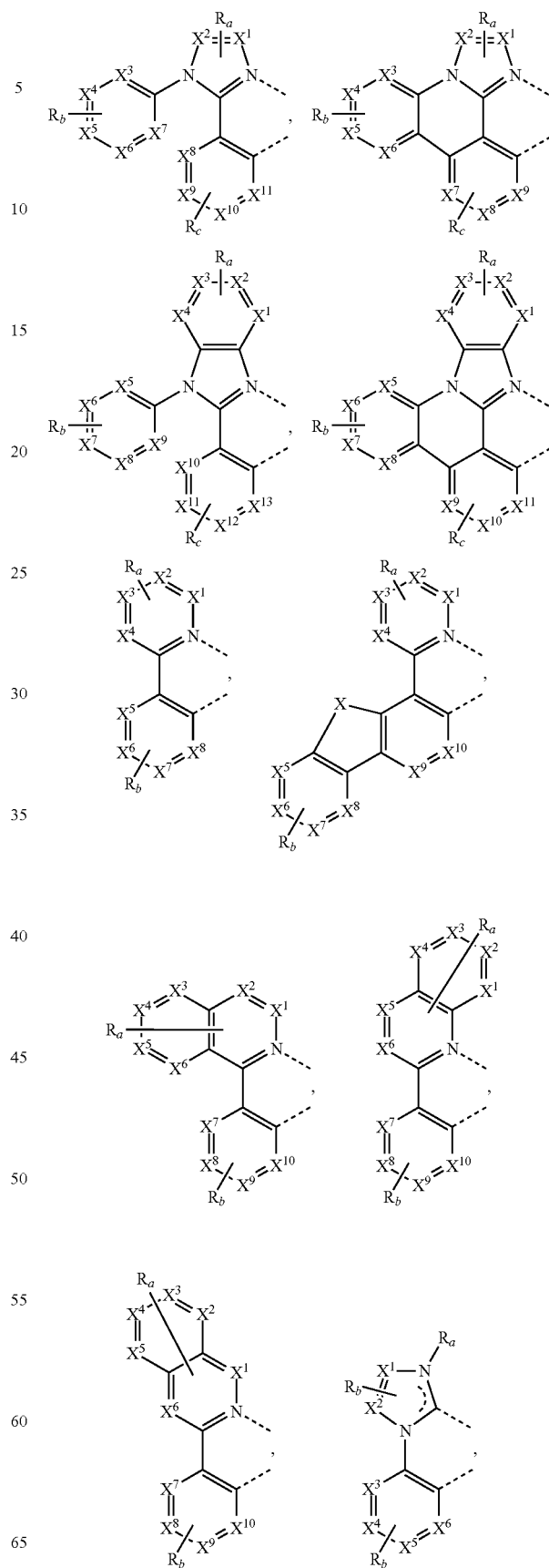
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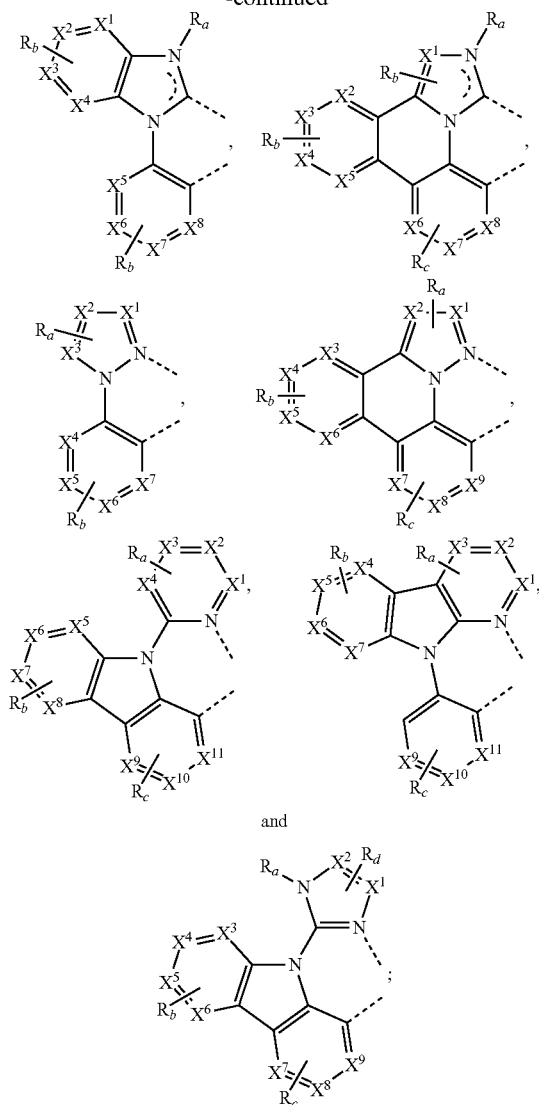
According to another embodiment, a first device comprising a first organic light emitting device is also provided. The first organic light emitting device can include an anode, a cathode, and an organic layer, disposed between the anode and the cathode. The organic layer can include a compound of the invention. The first device can be a consumer product, an organic light-emitting device, an electronic component module, and/or a lighting panel.

In one embodiment, the first device is selected from the group consisting of a consumer product, an electronic component module, an organic light-emitting device, and a lighting panel. In another embodiment, the organic layer is an emissive layer and the compound is a host. In another embodiment, the organic layer is an electron blocking layer, and the compound is an electron blocking material. In another embodiment, the organic layer is a transporting layer, and the compound is a transporting material.

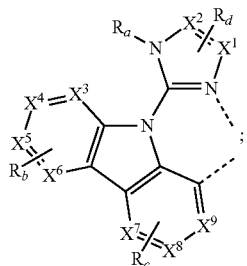
In one embodiment, the organic layer further comprises a phosphorescent emissive dopant; wherein the emissive dopant is a transition metal complex having at least one ligand or part of the ligand if the ligand is more than bidentate selected from the group consisting of:

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and



wherein each X<sup>1</sup> to X<sup>13</sup> are independently selected from the group consisting of carbon and nitrogen;

wherein X is selected from the group consisting of BR', NR', PR', O, S, Se, C=O, S=O, SO<sub>2</sub>, CR'R'', SiR''R'', and GeR''R'';

wherein R' and R'' are optionally fused or joined to form a ring;

wherein each R<sub>a</sub>, R<sub>b</sub>, R<sub>c</sub>, and R<sub>d</sub> may represent from mono substitution to the possible maximum number of substitution, or no substitution;

wherein R', R'', R<sub>a</sub>, R<sub>b</sub>, R<sub>c</sub>, and R<sub>d</sub> are each independently selected from the group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acids, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof; and

wherein any two adjacent substituents of R<sub>a</sub>, R<sub>b</sub>, R<sub>c</sub>, and R<sub>d</sub> are optionally fused or joined to form a ring or form a multidentate ligand.

According to one embodiment a formulation is provided comprising a compound of the invention.

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## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows an organic light emitting device.

FIG. 2 shows an inverted organic light emitting device that does not have a separate electron transport layer.

## DETAILED DESCRIPTION

Generally, an OLED comprises at least one organic layer disposed between and electrically connected to an anode and a cathode. When a current is applied, the anode injects holes and the cathode injects electrons into the organic layer(s). The injected holes and electrons each migrate toward the oppositely charged electrode. When an electron and hole localize on the same molecule, an "exciton," which is a localized electron-hole pair having an excited energy state, is formed. Light is emitted when the exciton relaxes via a photoemissive mechanism. In some cases, the exciton may be localized on an excimer or an exciplex. Non-radiative mechanisms, such as thermal relaxation, may also occur, but are generally considered undesirable.

The initial OLEDs used emissive molecules that emitted light from their singlet states ("fluorescence") as disclosed, for example, in U.S. Pat. No. 4,769,292, which is incorporated by reference in its entirety. Fluorescent emission generally occurs in a time frame of less than 10 nanoseconds.

More recently, OLEDs having emissive materials that emit light from triplet states ("phosphorescence") have been demonstrated. Baldo et al., "Highly Efficient Phosphorescent Emission from Organic Electroluminescent Devices," *Nature*, vol. 395, 151-154, 1998; ("Baldo-I") and Baldo et al., "Very high-efficiency green organic light-emitting devices based on electrophosphorescence," *Appl. Phys. Lett.*, vol. 75, No. 3, 4-6 (1999) ("Baldo-II"), which are incorporated by reference in their entireties. Phosphorescence is described in more detail in U.S. Pat. No. 7,279,704 which is incorporated by reference in its entirety.

FIG. 1 shows an organic light emitting device. The figures are not necessarily drawn to scale. Device 100 may include a substrate 110, an anode 115, a hole injection layer 120, a hole transport layer 125, an electron blocking layer 130, an emissive layer 135, a hole blocking layer 140, an electron transport layer 145, an electron injection layer 150, a protective layer 155, a cathode 160, and a barrier layer 170. Cathode 160 is a compound cathode having a first conductive layer 162 and a second conductive layer 164. Device 100 may be fabricated by depositing the layers described, in order. The properties and functions of these various layers, as well as example materials, are described in more detail in U.S. Pat. No. 7,279,704 which is incorporated by reference in its entirety.

More examples for each of these layers are available. For example, a flexible and transparent substrate-anode combination is disclosed in U.S. Pat. No. 5,844,363, which is incorporated by reference in its entirety. An example of a p-doped hole transport layer is m-MTDATA doped with F<sub>4</sub>-TCNQ at a molar ratio of 50:1, as disclosed in U.S. Patent Application Publication No. 2003/0230980, which is incorporated by reference in its entirety. Examples of emissive and host materials are disclosed in U.S. Pat. No. 6,303,238 to Thompson et al., which is incorporated by reference in its entirety. An example of an n-doped electron transport layer is BPhen doped with Li at a molar ratio of 1:1, as disclosed in U.S. Patent Application Publication No. 2003/0230980, which is incorporated by reference in its entirety. U.S. Pat. Nos. 5,703,436 and 5,707,745, which are incorporated by

reference in their entireties, disclose examples of cathodes including compound cathodes having a thin layer of metal such as Mg:Ag with an overlying transparent, electrically-conductive, sputter-deposited ITO layer. The theory and use of blocking layers is described in more detail in U.S. Pat. No. 6,097,147 and U.S. Patent Application Publication No. 2003/0230980, which are incorporated by reference in their entireties. Examples of injection layers are provided in U.S. Patent Application Publication No. 2004/0174116, which is incorporated by reference in its entirety. A description of protective layers may be found in U.S. Patent Application Publication No. 2004/0174116, which is incorporated by reference in its entirety.

FIG. 2 shows an inverted OLED 200. The device includes a substrate 210, a cathode 215, an emissive layer 220, a hole transport layer 225, and an anode 230. Device 200 may be fabricated by depositing the layers described, in order. Because the most common OLED configuration has a cathode disposed over the anode, and device 200 has cathode 215 disposed under anode 230, device 200 may be referred to as an "inverted" OLED. Materials similar to those described with respect to device 100 may be used in the corresponding layers of device 200. FIG. 2 provides one example of how some layers may be omitted from the structure of device 100.

The simple layered structure illustrated in FIGS. 1 and 2 is provided by way of non-limiting example, and it is understood that embodiments of the invention may be used in connection with a wide variety of other structures. The specific materials and structures described are exemplary in nature, and other materials and structures may be used. Functional OLEDs may be achieved by combining the various layers described in different ways, or layers may be omitted entirely, based on design, performance, and cost factors. Other layers not specifically described may also be included. Materials other than those specifically described may be used. Although many of the examples provided herein describe various layers as comprising a single material, it is understood that combinations of materials, such as a mixture of host and dopant, or more generally a mixture, may be used. Also, the layers may have various sublayers. The names given to the various layers herein are not intended to be strictly limiting. For example, in device 200, hole transport layer 225 transports holes and injects holes into emissive layer 220, and may be described as a hole transport layer or a hole injection layer. In one embodiment, an OLED may be described as having an "organic layer" disposed between a cathode and an anode. This organic layer may comprise a single layer, or may further comprise multiple layers of different organic materials as described, for example, with respect to FIGS. 1 and 2.

Structures and materials not specifically described may also be used, such as OLEDs comprised of polymeric materials (PLEDs) such as disclosed in U.S. Pat. No. 5,247,190 to Friend et al., which is incorporated by reference in its entirety. By way of further example, OLEDs having a single organic layer may be used. OLEDs may be stacked, for example as described in U.S. Pat. No. 5,707,745 to Forrest et al, which is incorporated by reference in its entirety. The OLED structure may deviate from the simple layered structure illustrated in FIGS. 1 and 2. For example, the substrate may include an angled reflective surface to improve out-coupling, such as a mesa structure as described in U.S. Pat. No. 6,091,195 to Forrest et al., and/or a pit structure as described in U.S. Pat. No. 5,834,893 to Bulovic et al., which are incorporated by reference in their entireties.

Unless otherwise specified, any of the layers of the various embodiments may be deposited by any suitable method. For the organic layers, preferred methods include thermal evaporation, ink-jet, such as described in U.S. Pat. Nos. 6,013,982 and 6,087,196, which are incorporated by reference in their entireties, organic vapor phase deposition (OVPD), such as described in U.S. Pat. No. 6,337,102 to Forrest et al., which is incorporated by reference in its entirety, and deposition by organic vapor jet printing (OVJP), such as described in U.S. Pat. No. 7,431,968, which is incorporated by reference in its entirety. Other suitable deposition methods include spin coating and other solution based processes. Solution based processes are preferably carried out in nitrogen or an inert atmosphere. For the other layers, preferred methods include thermal evaporation. Preferred patterning methods include deposition through a mask, cold welding such as described in U.S. Pat. Nos. 6,294,398 and 6,468,819, which are incorporated by reference in their entireties, and patterning associated with some of the deposition methods such as ink jet and OVJD. Other methods may also be used. The materials to be deposited may be modified to make them compatible with a particular deposition method. For example, substituents such as alkyl and aryl groups, branched or unbranched, and preferably containing at least 3 carbons, may be used in small molecules to enhance their ability to undergo solution processing. Substituents having 20 carbons or more may be used, and 3-20 carbons is a preferred range. Materials with asymmetric structures may have better solution processability than those having symmetric structures, because asymmetric materials may have a lower tendency to recrystallize. Dendrimer substituents may be used to enhance the ability of small molecules to undergo solution processing.

Devices fabricated in accordance with embodiments of the present invention may further optionally comprise a barrier layer. One purpose of the barrier layer is to protect the electrodes and organic layers from damaging exposure to harmful species in the environment including moisture, vapor and/or gases, etc. The barrier layer may be deposited over, under or next to a substrate, an electrode, or over any other parts of a device including an edge. The barrier layer may comprise a single layer, or multiple layers. The barrier layer may be formed by various known chemical vapor deposition techniques and may include compositions having a single phase as well as compositions having multiple phases. Any suitable material or combination of materials may be used for the barrier layer. The barrier layer may incorporate an inorganic or an organic compound or both. The preferred barrier layer comprises a mixture of a polymeric material and a non-polymeric material as described in U.S. Pat. No. 7,968,146, PCT Pat. Application Nos. PCT/US2007/023098 and PCT/US2009/042829, which are herein incorporated by reference in their entireties. To be considered a "mixture", the aforesaid polymeric and non-polymeric materials comprising the barrier layer should be deposited under the same reaction conditions and/or at the same time. The weight ratio of polymeric to non-polymeric material may be in the range of 95:5 to 5:95. The polymeric material and the non-polymeric material may be created from the same precursor material. In one example, the mixture of a polymeric material and a non-polymeric material consists essentially of polymeric silicon and inorganic silicon.

Devices fabricated in accordance with embodiments of the invention can be incorporated into a wide variety of electronic component modules (or units) that can be incorporated into a variety of electronic products or intermediate

components. Examples of such electronic products or intermediate components include display screens, lighting devices such as discrete light source devices or lighting panels, etc. that can be utilized by the end-user product manufacturers. Such electronic component modules can optionally include the driving electronics and/or power source(s). Devices fabricated in accordance with embodiments of the invention can be incorporated into a wide variety of consumer products that have one or more of the electronic component modules (or units) incorporated therein. Such consumer products would include any kind of products that include one or more light source(s) and/or one or more of some type of visual displays. Some examples of such consumer products include flat panel displays, computer monitors, medical monitors, televisions, billboards, lights for interior or exterior illumination and/or signaling, heads-up displays, fully or partially transparent displays, flexible displays, laser printers, telephones, cell phones, tablets, phablets, personal digital assistants (PDAs), laptop computers, digital cameras, camcorders, viewfinders, micro-displays, 3-D displays, vehicles, a large area wall, theater or stadium screen, or a sign. Various control mechanisms may be used to control devices fabricated in accordance with the present invention, including passive matrix and active matrix. Many of the devices are intended for use in a temperature range comfortable to humans, such as 18 degrees C. to 30 degrees C., and more preferably at room temperature (20-25 degrees C.), but could be used outside this temperature range, for example, from -40 degree C. to +80 degree C.

The materials and structures described herein may have applications in devices other than OLEDs. For example, other optoelectronic devices such as organic solar cells and organic photodetectors may employ the materials and structures. More generally, organic devices, such as organic transistors, may employ the materials and structures.

The term "halo," "halogen," or "halide" as used herein includes fluorine, chlorine, bromine, and iodine.

The term "alkyl" as used herein contemplates both straight and branched chain alkyl radicals. Preferred alkyl groups are those containing from one to fifteen carbon atoms and includes methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, and the like. Additionally, the alkyl group may be optionally substituted.

The term "cycloalkyl" as used herein contemplates cyclic alkyl radicals. Preferred cycloalkyl groups are those containing 3 to 7 carbon atoms and includes cyclopropyl, cyclopentyl, cyclohexyl, and the like. Additionally, the cycloalkyl group may be optionally substituted.

The term "alkenyl" as used herein contemplates both straight and branched chain alkene radicals. Preferred alkenyl groups are those containing two to fifteen carbon atoms. Additionally, the alkenyl group may be optionally substituted.

The term "alkynyl" as used herein contemplates both straight and branched chain alkyne radicals. Preferred alkynyl groups are those containing two to fifteen carbon atoms. Additionally, the alkynyl group may be optionally substituted.

The terms "aralkyl" or "arylalkyl" as used herein are used interchangeably and contemplate an alkyl group that has as a substituent an aromatic group. Additionally, the aralkyl group may be optionally substituted.

The term "heterocyclic group" as used herein contemplates aromatic and non-aromatic cyclic radicals. Hetero-aromatic cyclic radicals also means heteroaryl. Preferred hetero-non-aromatic cyclic groups are those containing 3 or

7 ring atoms which includes at least one hetero atom, and includes cyclic amines such as morpholino, piperidino, pyrrolidino, and the like, and cyclic ethers, such as tetrahydrofuran, tetrahydropyran, and the like. Additionally, the heterocyclic group may be optionally substituted.

The term "aryl" or "aromatic group" as used herein contemplates single-ring groups and polycyclic ring systems. The polycyclic rings may have two or more rings in which two carbons are common to two adjoining rings (the rings are "fused") wherein at least one of the rings is aromatic, e.g., the other rings can be cycloalkyls, cycloalkenyls, aryl, heterocycles, and/or heteroaryls. Additionally, the aryl group may be optionally substituted.

The term "heteroaryl" as used herein contemplates single-ring hetero-aromatic groups that may include from one to three heteroatoms, for example, pyrrole, furan, thiophene, imidazole, oxazole, thiazole, triazole, pyrazole, pyridine, pyrazine and pyrimidine, and the like. The term heteroaryl also includes polycyclic hetero-aromatic systems having two or more rings in which two atoms are common to two adjoining rings (the rings are "fused") wherein at least one of the rings is a heteroaryl, e.g., the other rings can be cycloalkyls, cycloalkenyls, aryl, heterocycles, and/or heteroaryls. Additionally, the heteroaryl group may be optionally substituted.

The alkyl, cycloalkyl, alkenyl, alkynyl, aralkyl, heterocyclic group, aryl, and heteroaryl may be optionally substituted with one or more substituents selected from the group consisting of hydrogen, deuterium, halogen, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, cyclic amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acid, ether, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof.

As used herein, "substituted" indicates that a substituent other than H is bonded to the relevant position, such as carbon. Thus, for example, where R<sup>1</sup> is mono-substituted, then one R<sup>1</sup> must be other than H. Similarly, where R<sup>1</sup> is di-substituted, then two of R<sup>1</sup> must be other than H. Similarly, where R<sup>1</sup> is unsubstituted, R<sup>1</sup> is hydrogen for all available positions.

The "aza" designation in the fragments described herein, i.e. aza-dibenzofuran, aza-dibenzothiophene, etc. means that one or more of the C—H groups in the respective fragment can be replaced by a nitrogen atom, for example, and without any limitation, azatriphenylene encompasses both dibenzo[f,h]quinoxaline and dibenzo[f,h]quinoline. One of ordinary skill in the art can readily envision other nitrogen analogs of the aza-derivatives described above, and all such analogs are intended to be encompassed by the terms as set forth herein.

It is to be understood that when a molecular fragment is described as being a substituent or otherwise attached to another moiety, its name may be written as if it were a fragment (e.g. phenyl, phenylene, naphthyl, dibenzofuryl) or as if it were the whole molecule (e.g. benzene, naphthalene, dibenzofuran). As used herein, these different ways of designating a substituent or attached fragment are considered to be equivalent.

The present invention provides a series of metallocene containing materials that are superior materials to those used in current OLED devices, particularly when used as electron-blocking layer (EBL) materials. To achieve efficient and stable OLEDs, a balanced charge carrier transport and a broad recombination zone are required. This task can be accomplished by the design of bipolar host materials. In bipolar host materials, holes and electrons are transported

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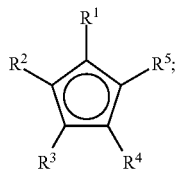
through different parts of the molecule. The hole transport in many cases occurs through carbazole units, whereas electron transport is often realized by the use of electron accepting N-heterocycles such as triazines or oxadiazoles. As described herein, a metallocene moiety was introduced to improve the hole transport, which improves OLED device performance parameters, such as efficiency and lifetime. Compared to conventional organic host compounds, metallocenes undergo a reversible one-electron oxidation at a lower potential. For example, osmocene undergoes a one electron oxidation around 0.4 V vs Fc+/Fc (see Organometallic 1995, 14, 4879, which is incorporated by reference herein in its entirety), while carbazole undergoes a one electron oxidation around 0.9 V vs Fc+/Fc. The shallower HOMO of osmocene improves the hole transport or hole trapping property in the device.

Compounds of the Invention:

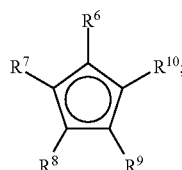
The compounds of the present invention may be synthesized using techniques well-known in the art of organic synthesis. The starting materials and intermediates required for the synthesis may be obtained from commercial sources or synthesized according to methods known to those skilled in the art.

In one aspect, the compound of the invention is a compound comprising an osmocene structure having a formula of  $\text{Os}(\text{L}^1)(\text{L}^2)$ ;

wherein  $\text{L}^1$  has the formula:



wherein  $\text{L}^2$  has the formula:



wherein  $\text{R}^1$  to  $\text{R}^{10}$  are each independently selected from the group consisting of hydrogen, deuterium, halogen, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, heterocyclyl, acyl, carbonyl, carboxylic acid, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof, and wherein at least one of  $\text{R}^1$  to  $\text{R}^{10}$  comprises an aryl group or a heteroaryl group.

The structures of  $\text{R}^1$  to  $\text{R}^{10}$  are not particularly limited, as long as at least one of  $\text{R}^1$  to  $\text{R}^{10}$  comprises an aryl group or a heteroaryl group. In one embodiment,  $\text{R}^1$  to  $\text{R}^{10}$  are each independently selected from the group consisting of hydrogen, deuterium, halogen, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, heterocyclyl, acyl, carbonyl, carboxylic acid, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof.

The size and/or the number of carbon atoms in the aryl group or the heteroaryl group is not particularly limited. In

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one embodiment, at least one of  $\text{R}^1$  to  $\text{R}^{10}$  comprises an aryl group having at least 12 carbon atoms or a heteroaryl group having at least 4 carbon atoms.

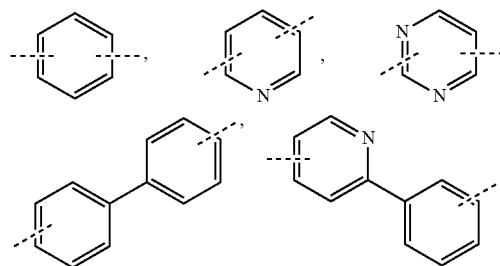
In one embodiment, at least one of  $\text{R}^1$  to  $\text{R}^{10}$  comprises a heteroaryl group. Any heteroaryl group is contemplated within the invention. In one embodiment, at least one of  $\text{R}^1$  to  $\text{R}^{10}$  comprises at least one chemical group selected from the group consisting of dibenzothiophene, dibenzofuran, dibenzoselenophene, furan, thiophene, benzofuran, benzothiophene, benzoselenophene, carbazole, indolocarbazole, pyridylindole, pyrrolodipyridine, pyrazole, imidazole, triazole, oxazole, thiazole, oxadiazole, oxatriazole, dioxazole, thiadiazole, pyridine, pyridazine, pyrimidine, pyrazine, triazine, oxazine, oxathiazine, oxadiazine, indole, benzimidazole, indazole, indoxazine, benzoxazole, benzisoxazole, benzothiazole, quinoline, isoquinoline, cinnoline, quinoxaline, naphthyridine, phthalazine, pteridine, xanthene, acridine, phenazine, phenothiazine, phenoxazine, benzofuropyridine, furodipyridine, benzothienopyridine, thienodipyridine, benzoselenophenopyridine, selenophenodipyridine, aza analogs thereof, and combinations thereof. In one embodiment, at least one of  $\text{R}^1$  to  $\text{R}^{10}$  comprises at least one carbazole group.

In one embodiment, at least one of  $\text{R}^1$  to  $\text{R}^{10}$  comprises an aryl group. Any aryl group is contemplated within the invention. In one embodiment, at least one of  $\text{R}^1$  to  $\text{R}^{10}$  comprises at least one chemical group selected from the group consisting of biphenyl, triphenyl, triphenylene, naphthalene, anthracene, phenalene, phenanthrene, fluorene, pyrene, chrysene, perylene, and azulene.

In one embodiment, at least one of  $\text{R}^1$  to  $\text{R}^{10}$  comprises at least one chemical group selected from the group consisting of triphenylene, carbazole, dibenzothiophene, dibenzofuran, dibenzoselenophene, azatriphenylene, azacarbazole, aza-dibenzothiophene, aza-dibenzofuran, and aza-dibenzoselenophene.

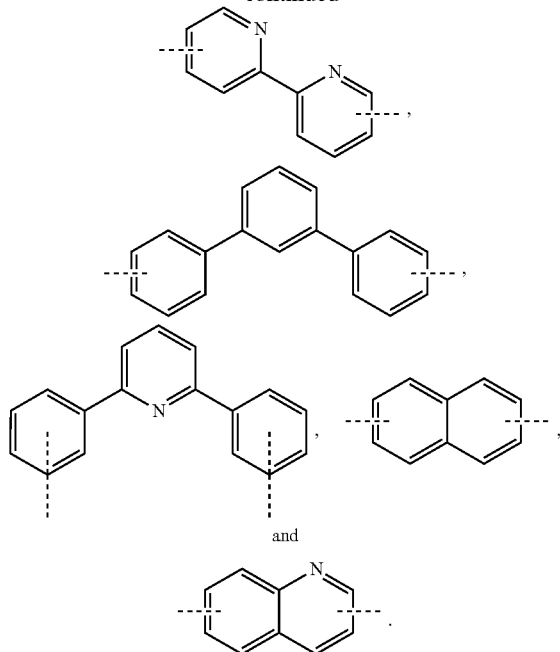
In some embodiments, at least one of  $\text{R}^1$  to  $\text{R}^{10}$  is L-G. The structure of L is not particularly limited. In one embodiment, L is a direct bond. In another embodiment, L is an organic linker. In one embodiment, the organic linker is an alkyl group, wherein the alkyl group may be saturated or unsaturated and may be optionally substituted. In another embodiment, L is comprised of at least one ring, wherein the ring may be optionally substituted. In one embodiment, L is comprised of an aryl group. In another embodiment, L is comprised of a heteroaryl group. In some embodiments, L is comprised of one, two, three, or four or more rings. In one embodiment, the ring is a polycyclic structure. In one embodiment, the linker L is selected from the group consisting of:

Direct bond,



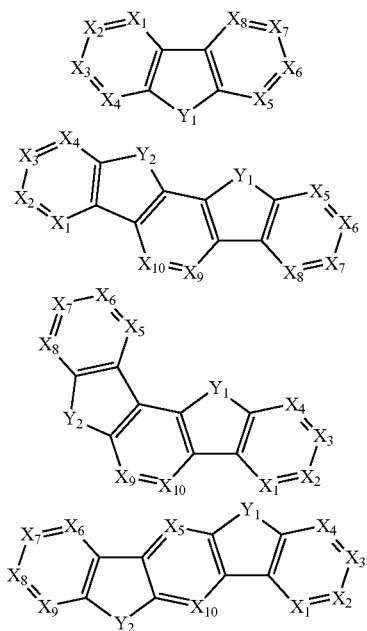
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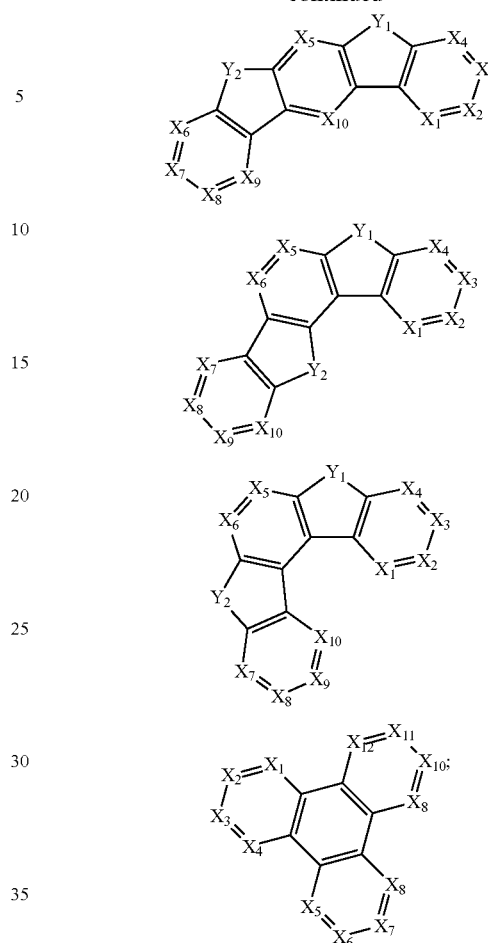


The structure of G is not particularly limited. In one embodiment, G comprises a ring, wherein the ring may be optionally substituted. In one embodiment, G comprises an aryl group. In another embodiment, G comprises a heterocyclic group. In another embodiment, G comprises a heteroaryl group. In one embodiment, G comprises one or more mono or polycyclic structures. In some embodiments, G is a polycyclic structure comprising two, three, four, five, or six or more rings. In one embodiment, G is a polycyclic structure comprising both all-carbon and heterocyclic rings.

In one embodiment, at least one of  $R^1$  to  $R^{10}$  is L-G; wherein L is a direct bond or an organic linker; and wherein G is selected from the group consisting of:

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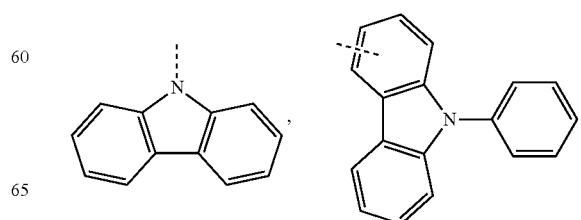
wherein  $Y_1$  and  $Y_2$  are independently selected from the group consisting of  $NR^{11}$ ,  $CR^{11}R^{12}$ , O, S, and Se;

wherein  $X_1$  to  $X_{12}$  are independently selected from the group consisting of  $CR^{13}$  and N;

wherein  $R^{11}$ ,  $R^{12}$ , and  $R^{13}$  are each independently selected from the group consisting of hydrogen, deuterium, halogen, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acid, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof, and

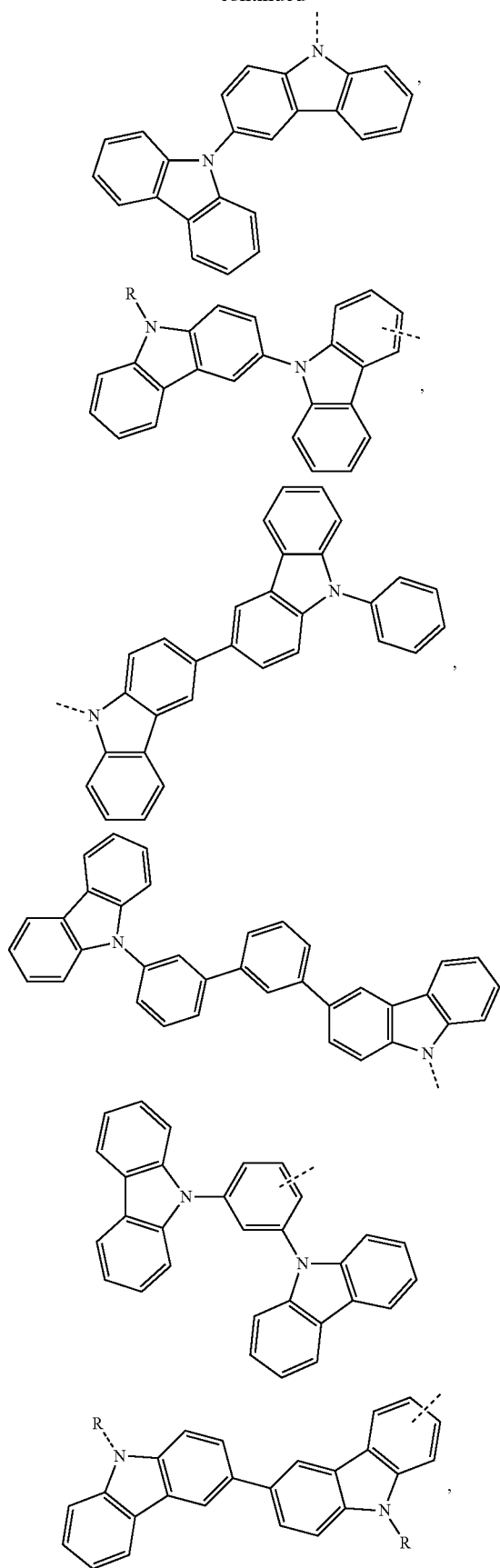
wherein any two adjacent substituents of  $R^{11}$ ,  $R^{12}$ , and  $R^{13}$  are optionally fused or joined to form a ring.

In one embodiment, G is selected from the group consisting of:

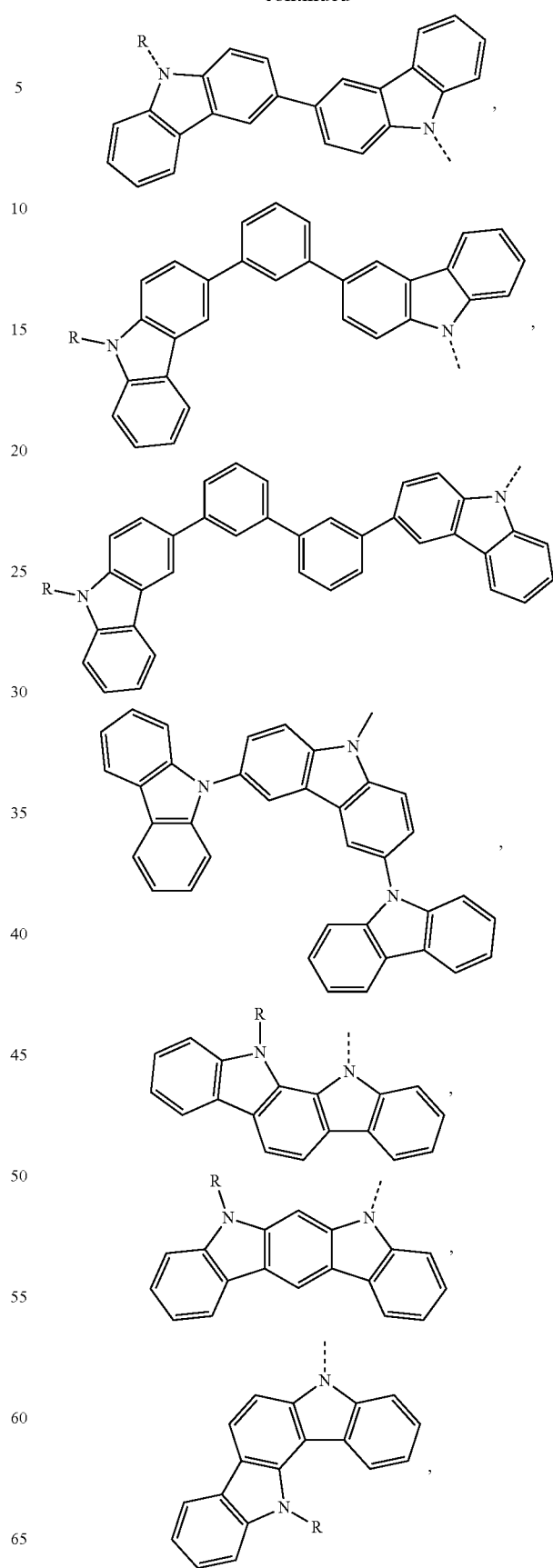


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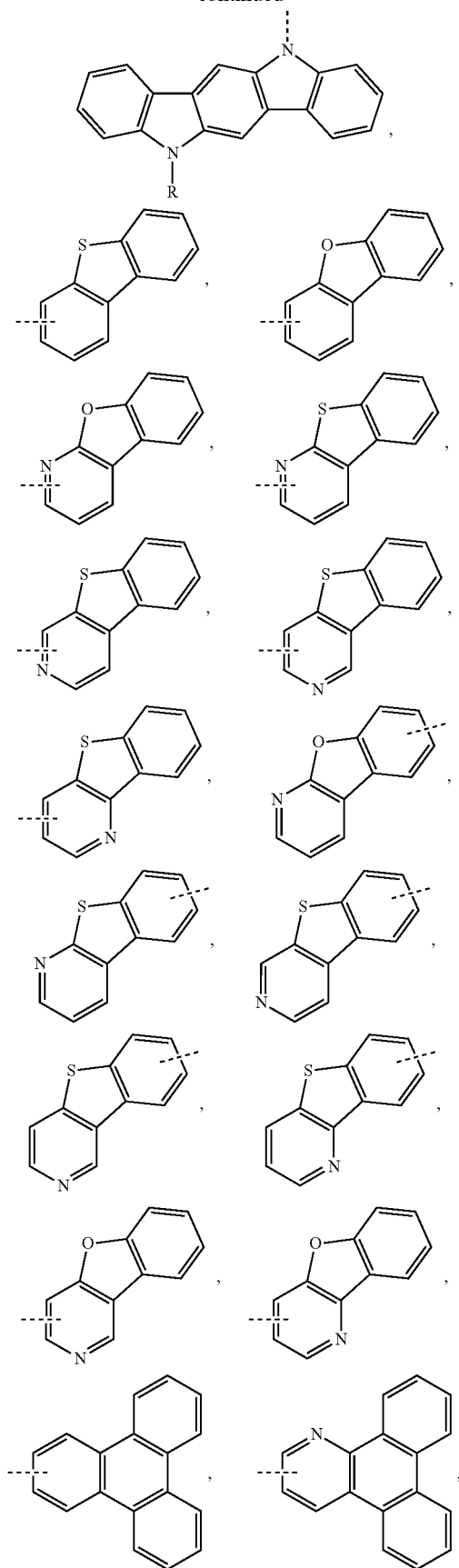
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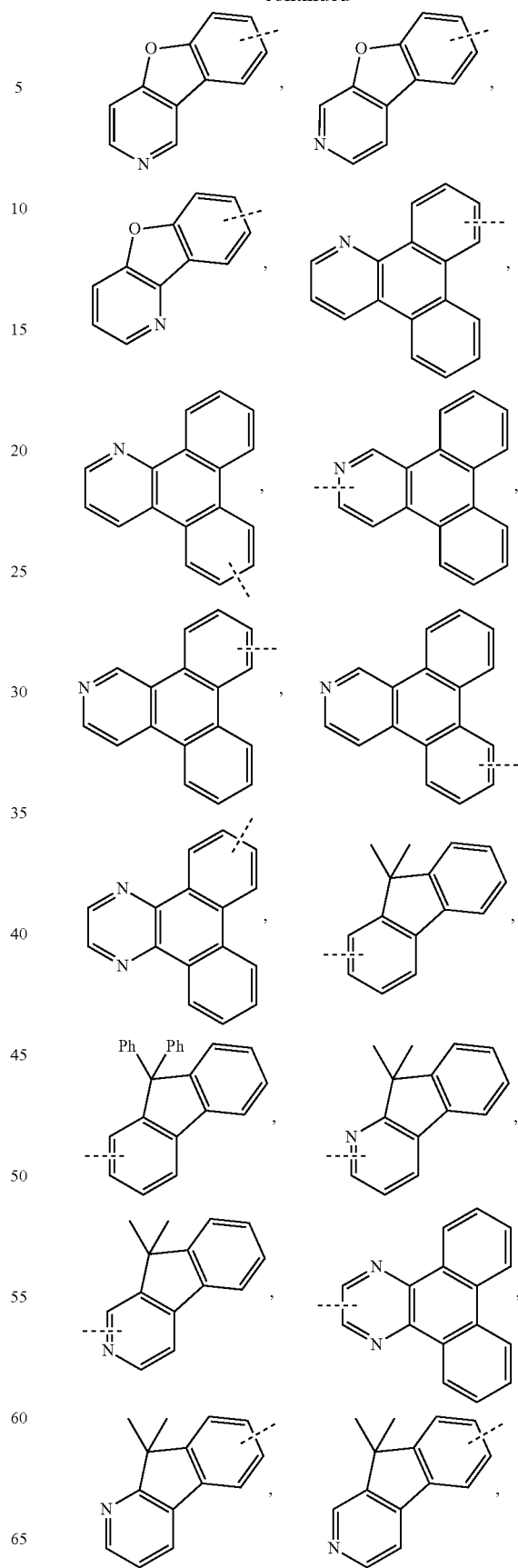


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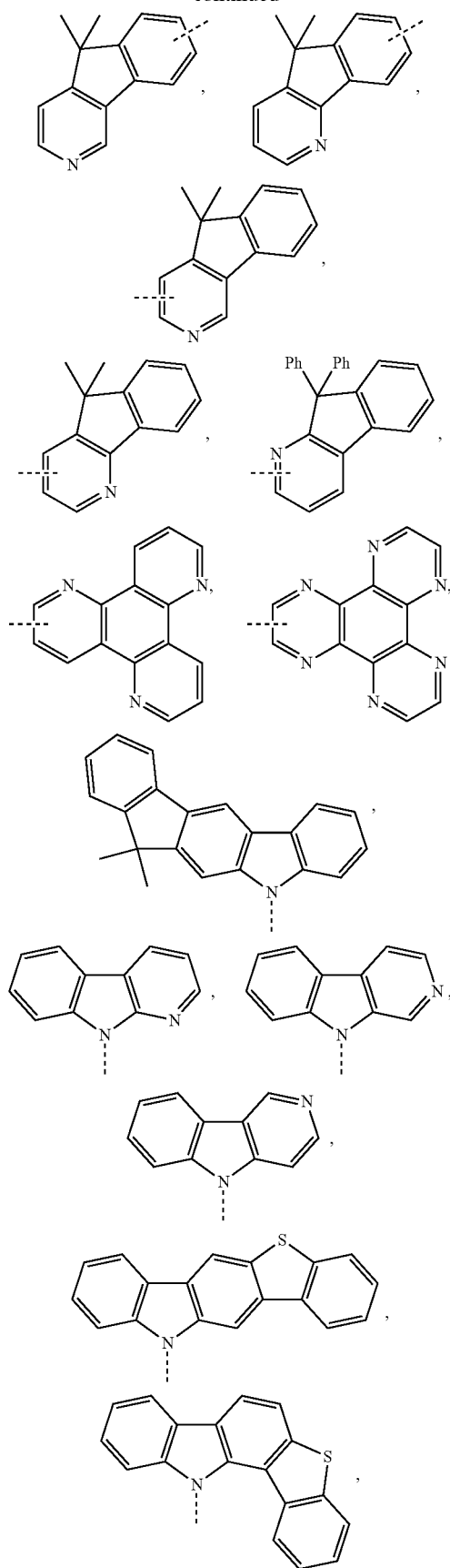
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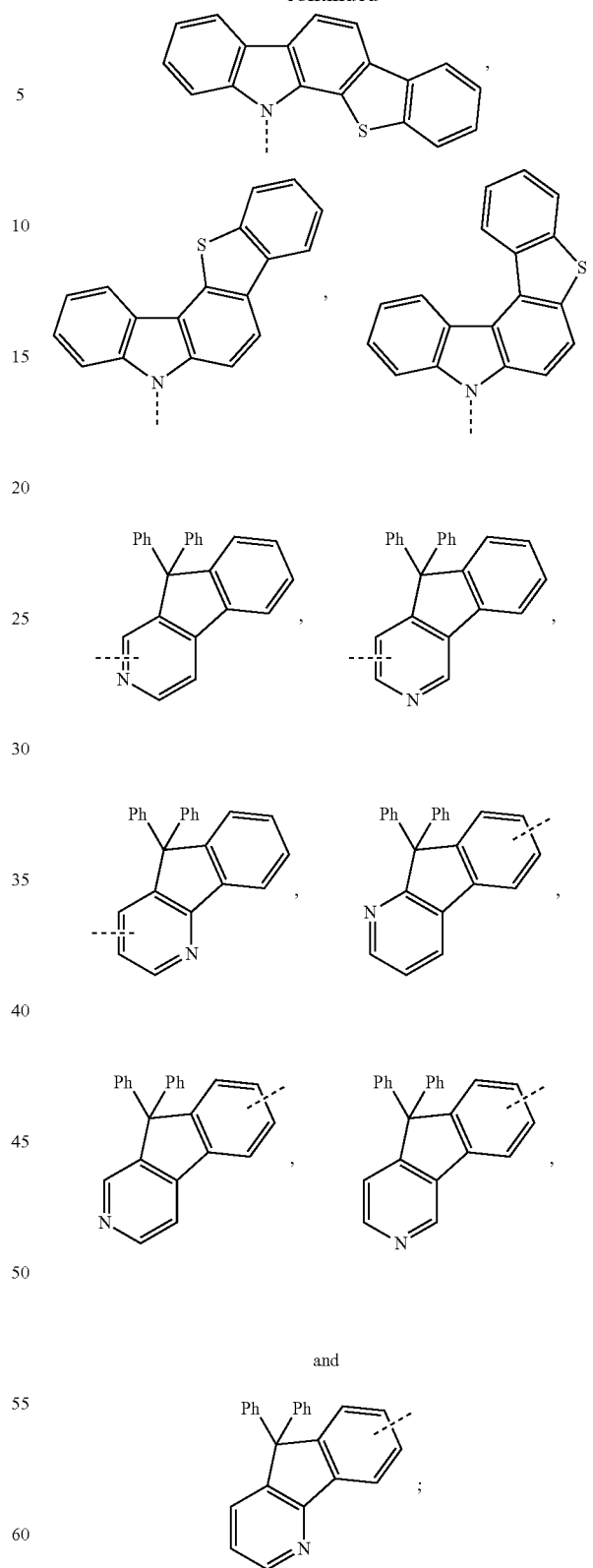


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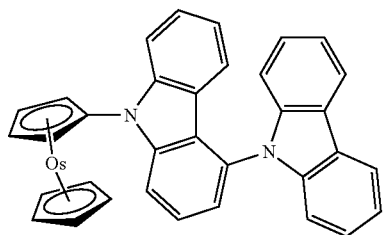
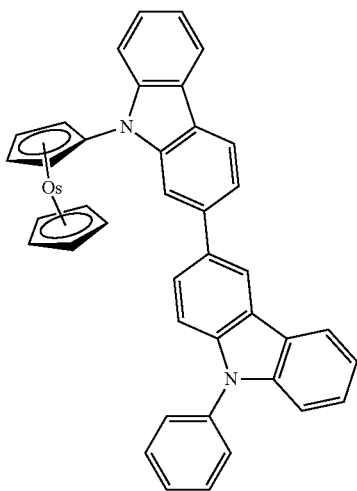
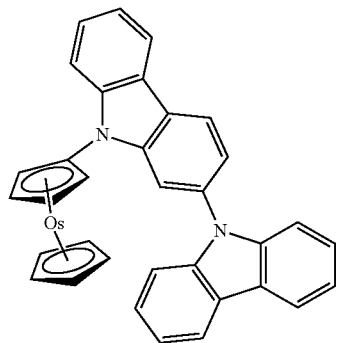
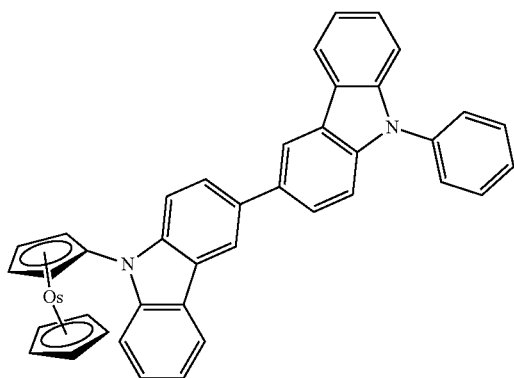


and

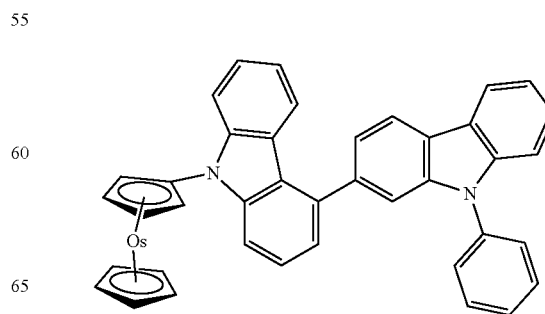
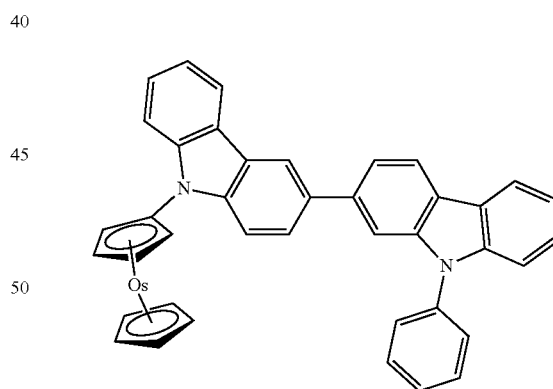
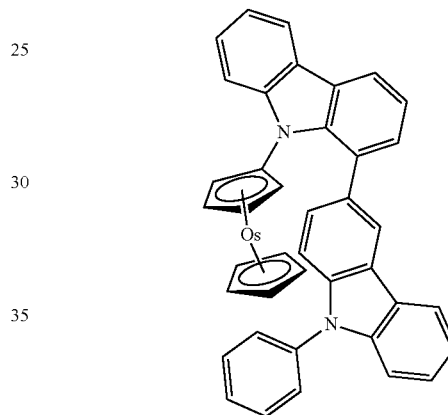
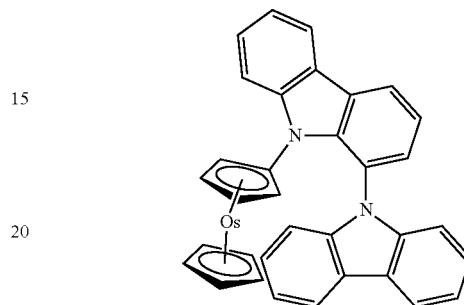
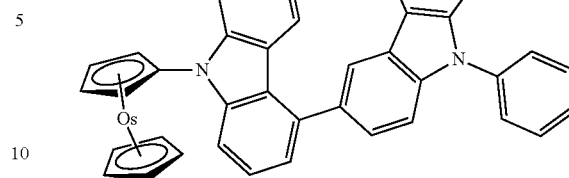
wherein R is selected from the group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, aryl-  
 65 alkyl, alkoxy, aryl, heteroaryl, aryloxy, amino, and combinations thereof.

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In one embodiment, the compound is selected from the group consisting of:

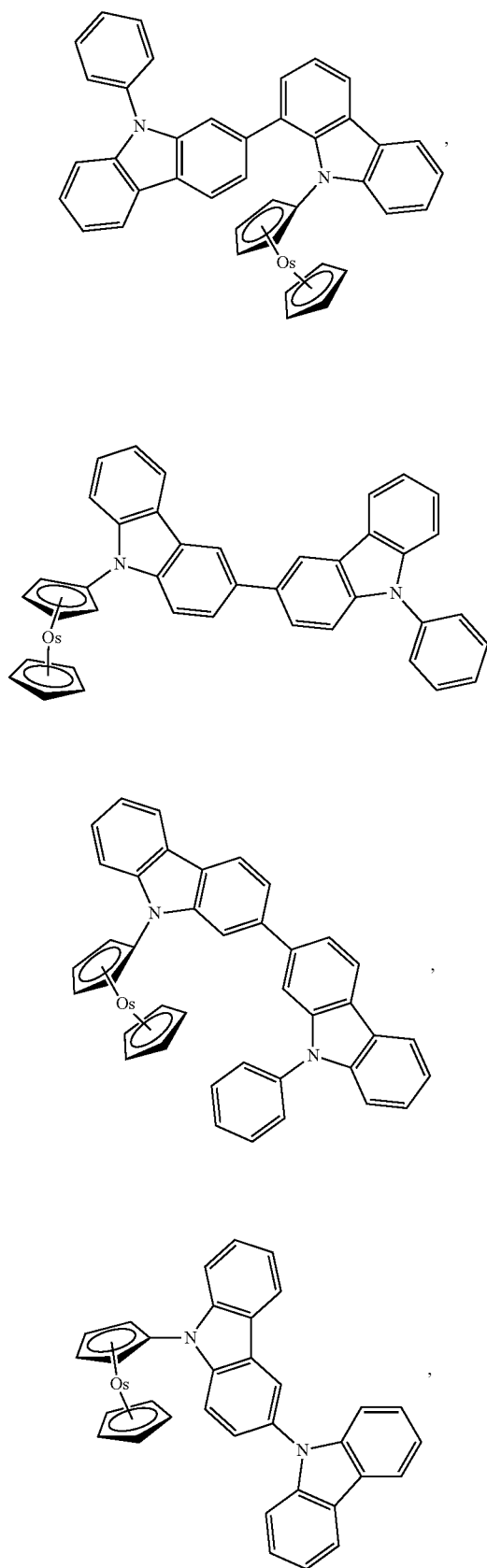
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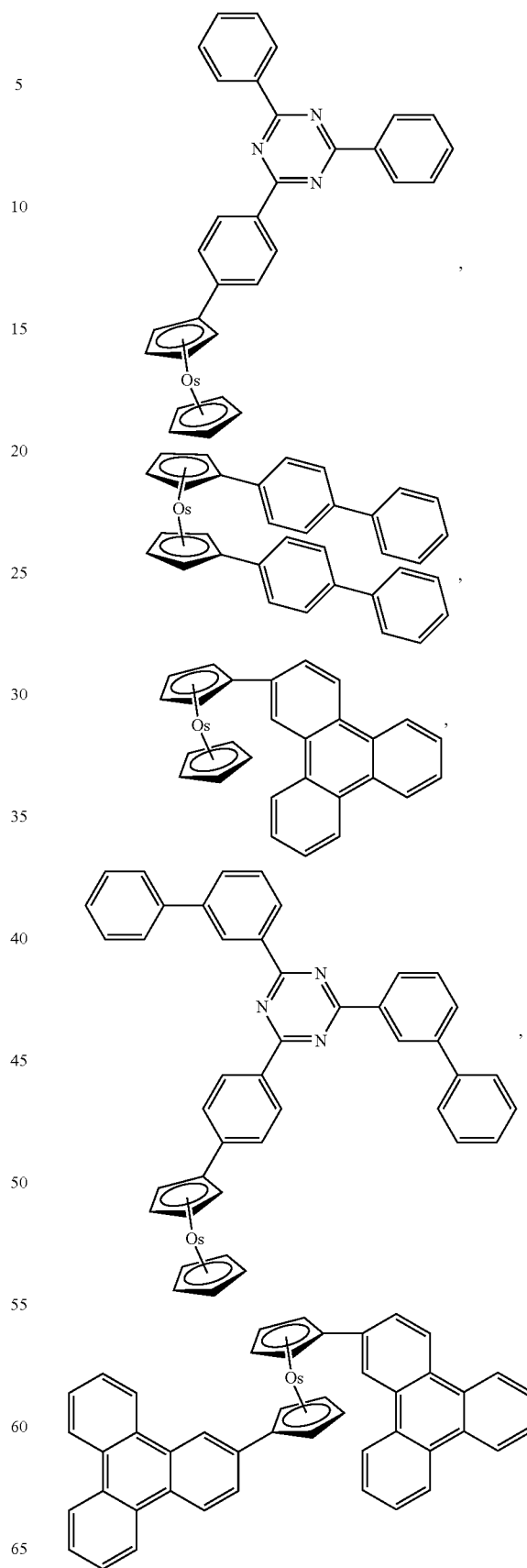


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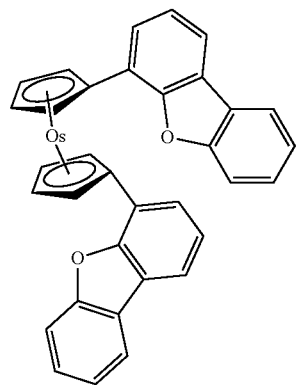
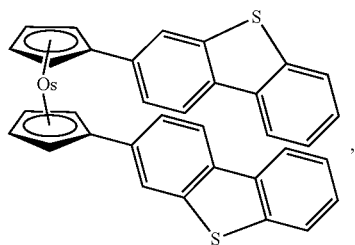
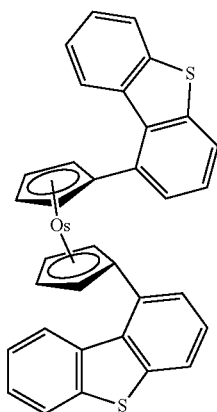
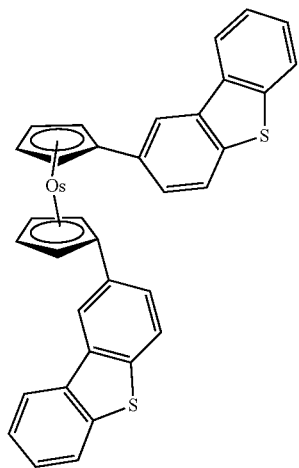
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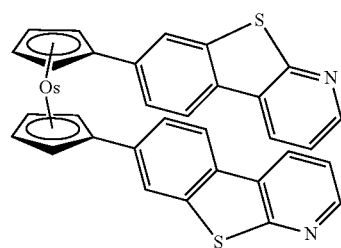
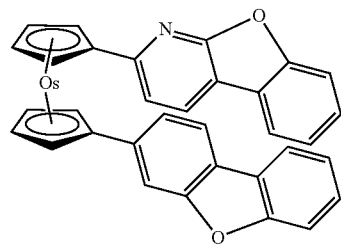
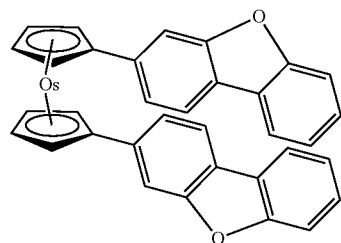
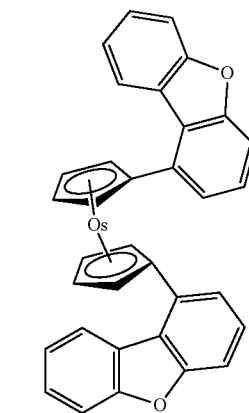
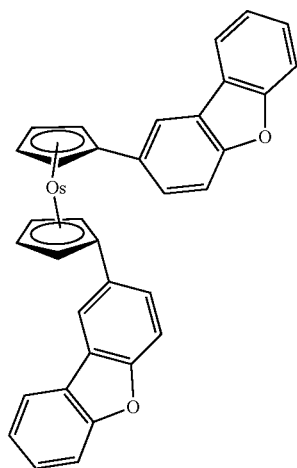
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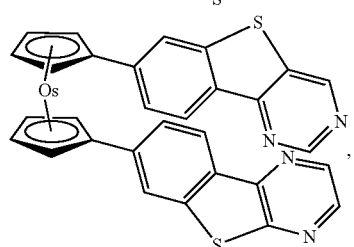
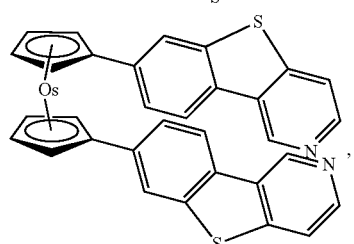
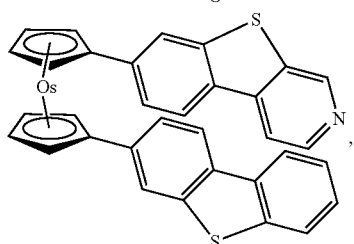
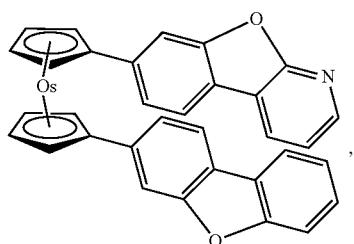
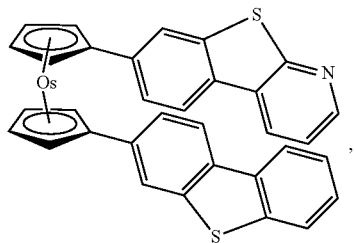
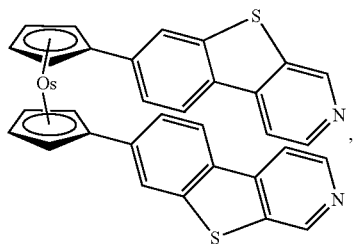
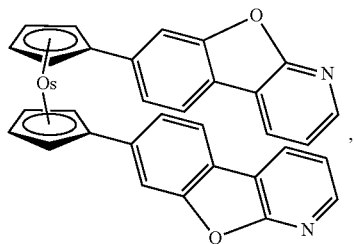
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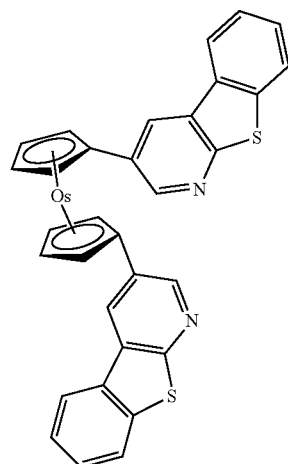
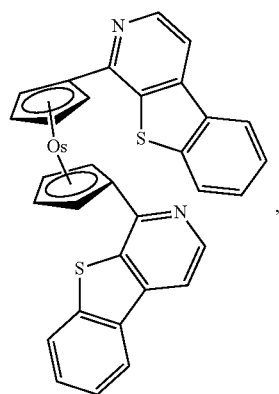
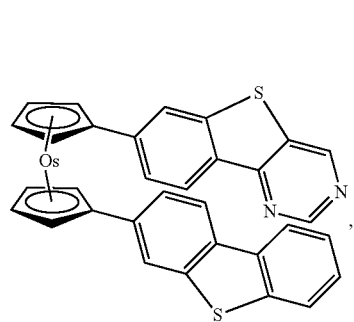
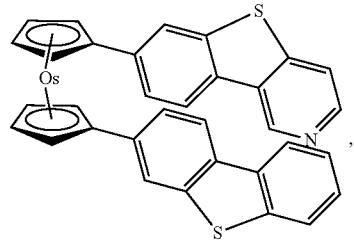
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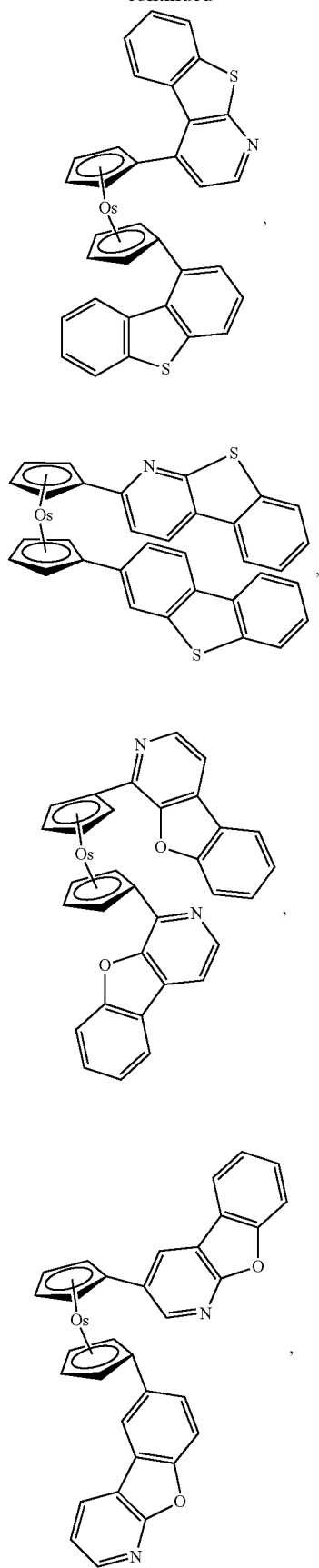
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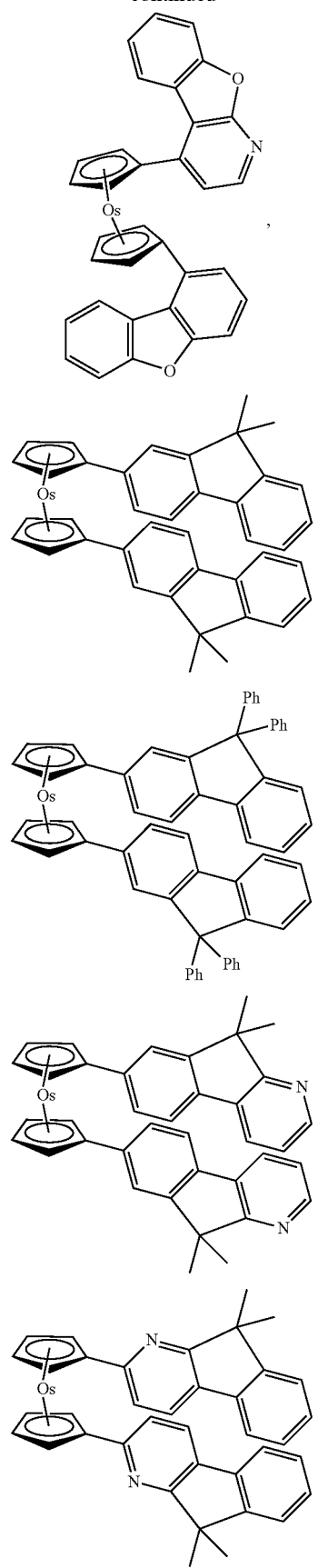
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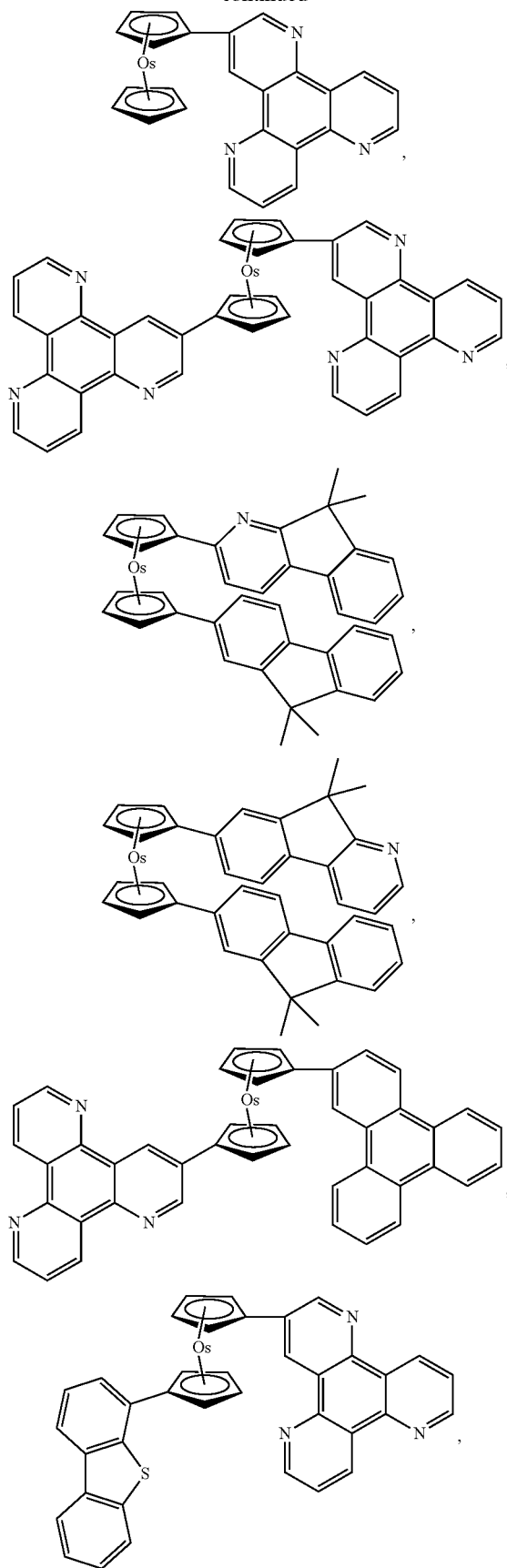
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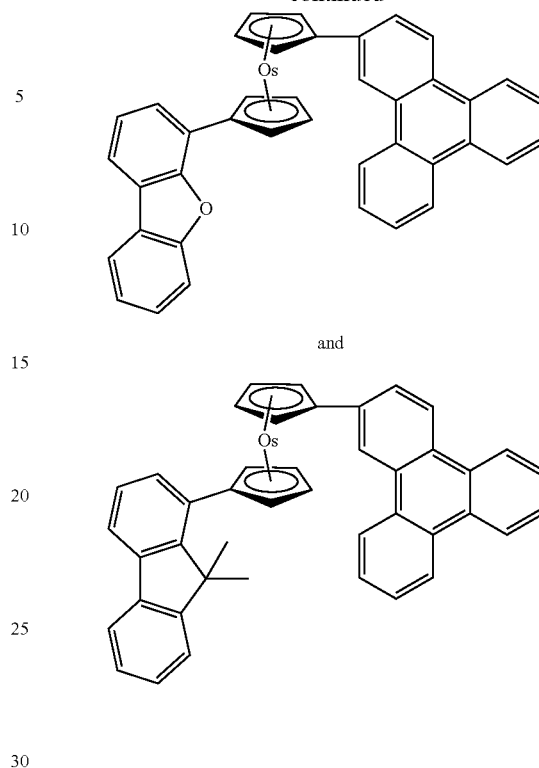


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**52**

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and

In some embodiments, the compound can be an emissive dopant. In some embodiments, the compound can produce emissions via phosphorescence, fluorescence, thermally activated delayed fluorescence, i.e., TADF (also referred to as E-type delayed fluorescence), triplet-triplet annihilation, or combinations of these processes.

Devices:

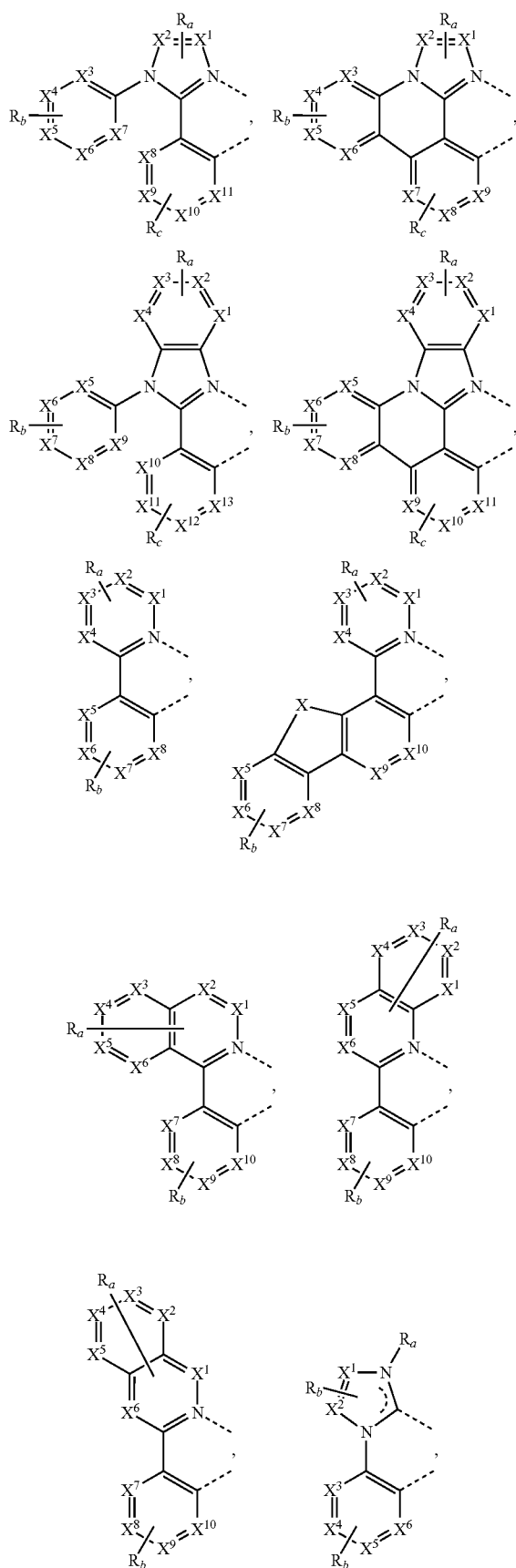
According to another aspect of the present disclosure, a first device is also provided. The first device includes a first organic light emitting device, that includes an anode, a cathode, and an organic layer disposed between the anode and the cathode. The organic layer may include a host and a phosphorescent dopant. The emissive layer can include a compound of the invention, and its variations as described herein.

The first device can be one or more of a consumer product, an electronic component module, an organic light-emitting device and a lighting panel. The organic layer can be an emissive layer and the compound can be an emissive dopant in some embodiments, while the compound can be a non-emissive dopant in other embodiments. The organic layer can be a charge transporting layer and the compound can be a charge transporting material in the organic layer in some embodiments. The organic layer can be a blocking layer and the compound can be a blocking material in the organic layer in some embodiments. The organic layer can be an emissive layer and the compound can be a host in some embodiments.

In one embodiment, the organic layer further comprises a phosphorescent emissive dopant; wherein the emissive dopant is a transition metal complex having at least one ligand, or part of the ligand if the ligand is more than bidentate, selected from the group consisting of:

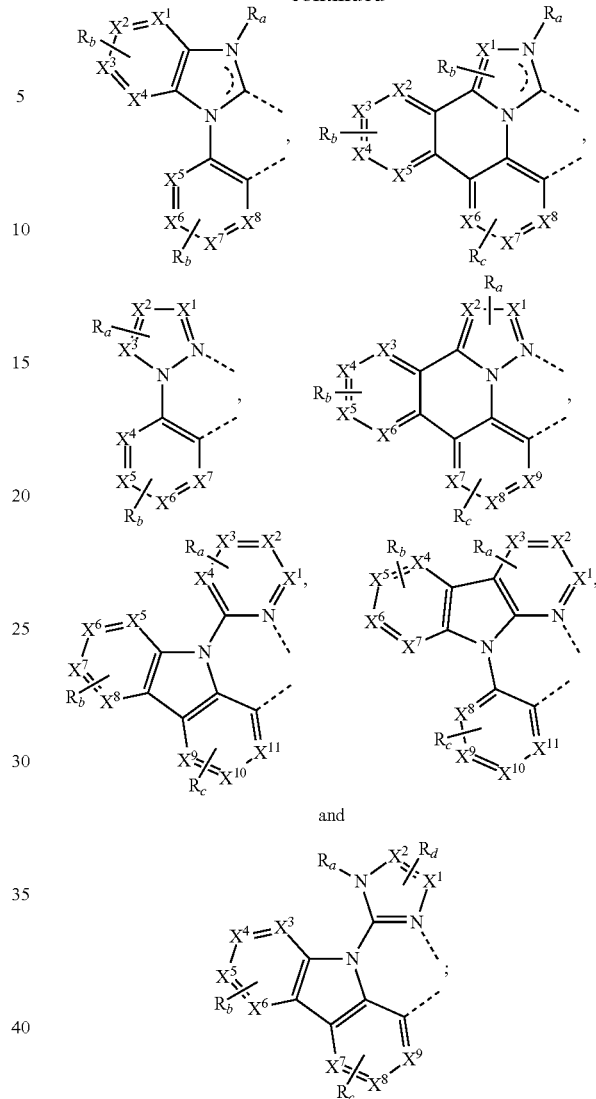


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and

wherein each  $X^1$  to  $X^{13}$  are independently selected from the group consisting of carbon and nitrogen;

wherein  $X$  is selected from the group consisting of  $BR'$ ,  $NR'$ ,  $PR'$ ,  $O$ ,  $S$ ,  $Se$ ,  $C=O$ ,  $S=O$ ,  $SO_2$ ,  $CR'R''$ ,  $SiR'R''$ , and  $GeR'R''$ ;

wherein  $R'$  and  $R''$  are optionally fused or joined to form a ring;

wherein each  $R_a$ ,  $R_b$ ,  $R_c$ , and  $R_d$  may represent from mono substitution to the possible maximum number of substitution, or no substitution;

wherein  $R'$ ,  $R''$ ,  $R_a$ ,  $R_b$ ,  $R_c$ , and  $R_d$  are each independently selected from the group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acids, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof; and

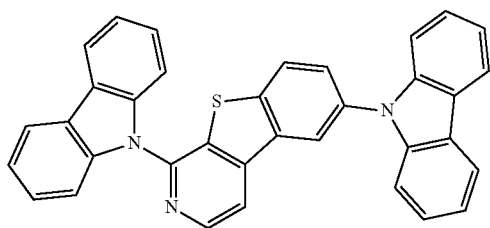
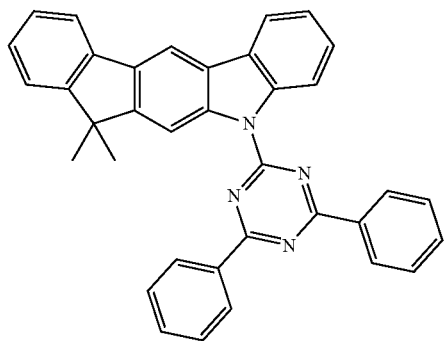
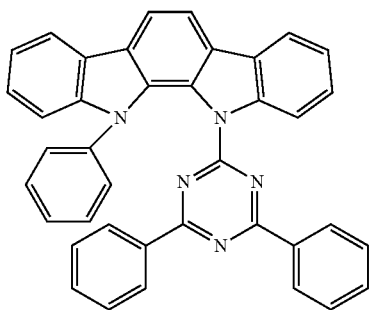
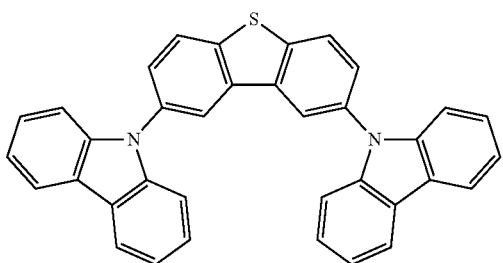
wherein any two adjacent substituents of  $R_a$ ,  $R_b$ ,  $R_c$ , and  $R_d$  are optionally fused or joined to form a ring or form a multidentate ligand.

The organic layer can also include a host. In some embodiments, the host can include a metal complex. The

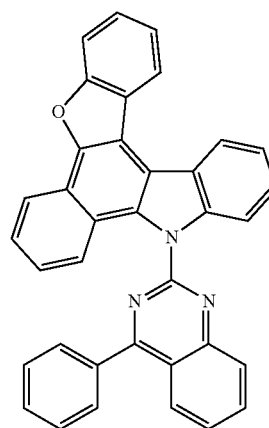
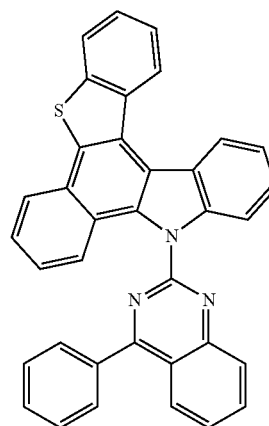
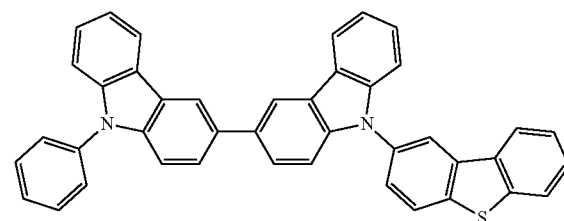
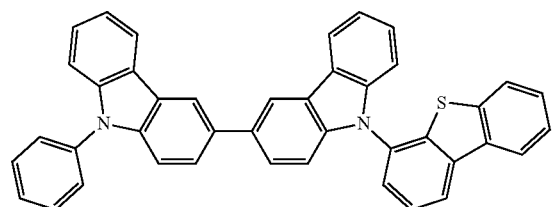
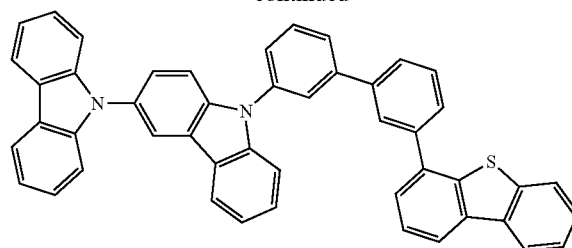
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host can be a triphenylene containing benzo-fused thiophene or benzo-fused furan. Any substituent in the host can be an unfused substituent independently selected from the group consisting of  $C_nH_{2n+1}$ ,  $OC_nH_{2n+1}$ ,  $OAr_1$ ,  $N(C_nH_{2n+1})_2$ ,  $N(Ar_1)(Ar_2)$ ,  $CH=CH-C_nH_{2n+1}$ ,  $C\equiv C-C_nH_{2n+1}$ ,  $Ar_1$ ,  $Ar_1-Ar_2$ , and  $C_nH_{2n}-Ar_1$ , or no substitution. In the preceding substituents  $n$  can range from 1 to 10; and  $Ar_1$  and  $Ar_2$  can be independently selected from the group consisting of benzene, biphenyl, naphthalene, triphenylene, carbazole, and heteroaromatic analogs thereof.

The host can be a compound comprising at least one chemical group selected from the group consisting of triphenylene, carbazole, dibenzothiophene, dibenzofuran, dibenzoselenophene, azatriphenylene, azacarbazole, aza-dibenzothiophene, aza-dibenzofuran, and aza-dibenzoselenophene. The host can include a metal complex. The host can be a specific compound selected from the group consisting of:

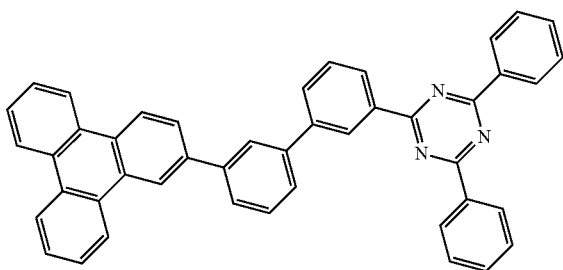
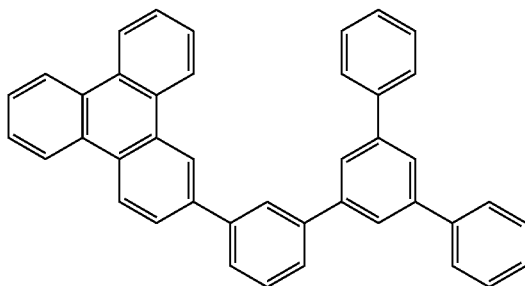
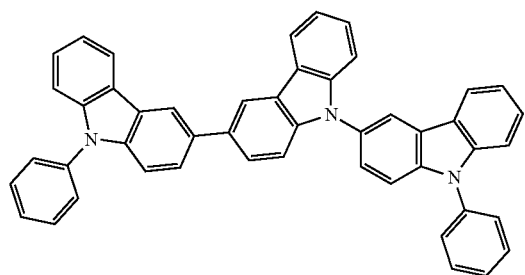
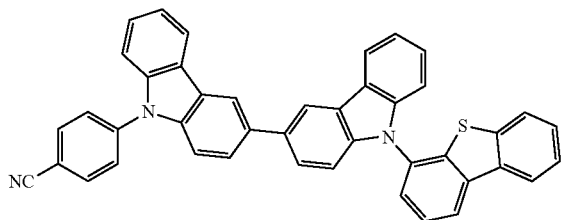
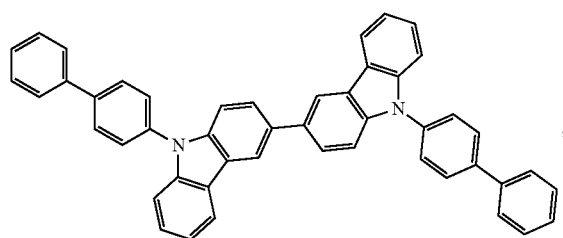
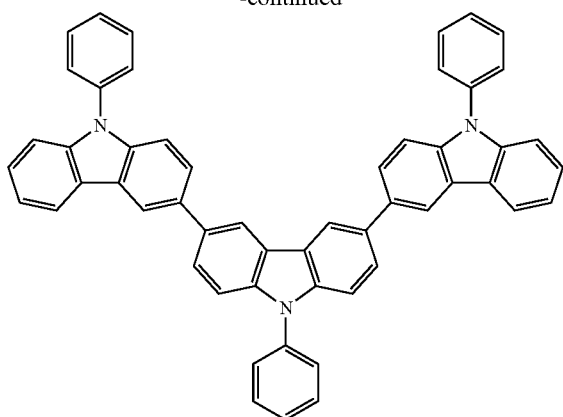
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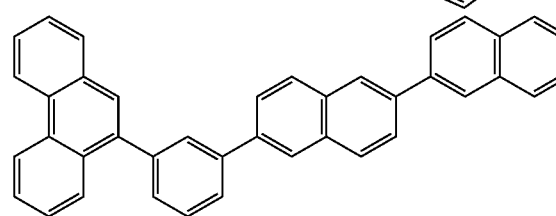
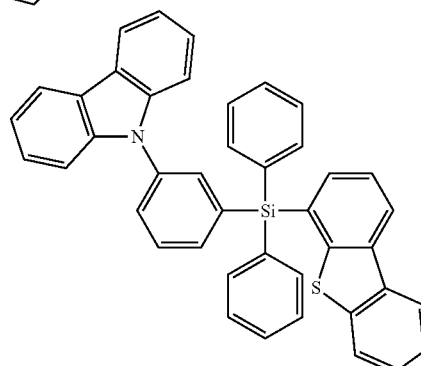
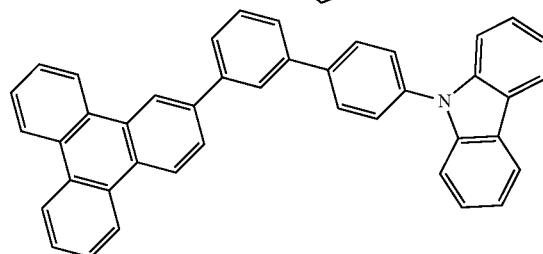
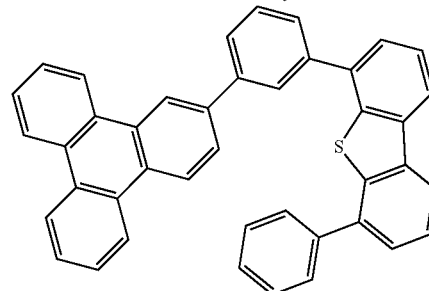
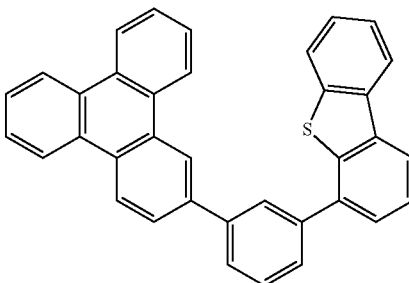
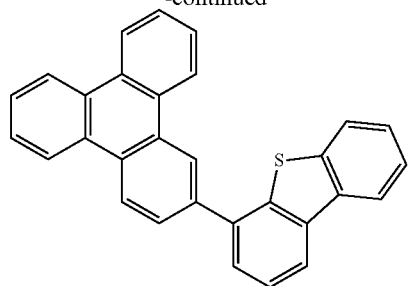


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and combinations thereof.

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## Formulations:

In yet another aspect of the present disclosure, a formulation that comprises a compound of the invention is described. The formulation can include one or more components selected from the group consisting of a solvent, a host, a hole injection material, hole transport material, and an electron transport layer material, disclosed herein.

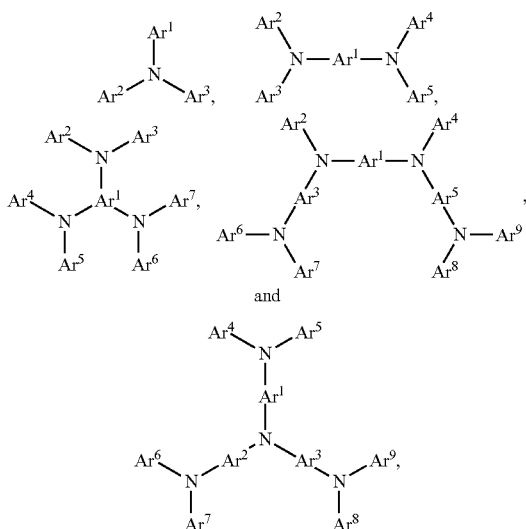
## Combination with Other Materials

The materials described herein as useful for a particular layer in an organic light emitting device may be used in combination with a wide variety of other materials present in the device. For example, emissive dopants disclosed herein may be used in conjunction with a wide variety of hosts, transport layers, blocking layers, injection layers, electrodes and other layers that may be present. The materials described or referred to below are non-limiting examples of materials that may be useful in combination with the compounds disclosed herein, and one of skill in the art can readily consult the literature to identify other materials that may be useful in combination.

## HIL/HTL:

A hole injecting/transporting material to be used in the present invention is not particularly limited, and any compound may be used as long as the compound is typically used as a hole injecting/transporting material. Examples of the material include, but are not limited to: a phthalocyanine or porphyrin derivative; an aromatic amine derivative; an indolocarbazole derivative; a polymer containing fluorohydrocarbon; a polymer with conductivity dopants; a conducting polymer, such as PEDOT/PSS; a self-assembly monomer derived from compounds such as phosphonic acid and silane derivatives; a metal oxide derivative, such as  $\text{MoO}_x$ ; a p-type semiconducting organic compound, such as 1,4,5,8,9,12-Hexaazatriphenylenehexacarbonitrile; a metal complex, and cross-linkable compounds.

Examples of aromatic amine derivatives used in HIL or HTL include, but are not limited to the following general structures:

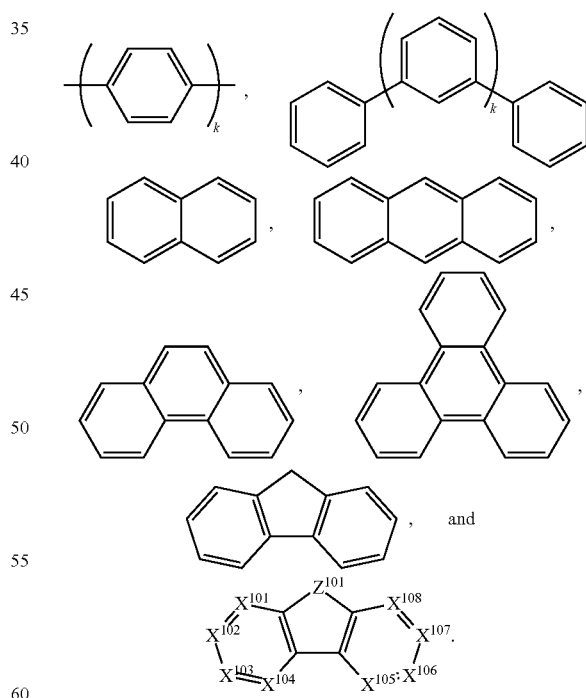


wherein each of  $\text{Ar}^1$  to  $\text{Ar}^9$  is selected from the group consisting of aromatic hydrocarbon cyclic compounds such as benzene, biphenyl, triphenyl, triphenylene, naphthalene, anthracene, phenalene, phenanthrene, fluorene, pyrene,

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chrysene, perylene, and azulene; the group consisting of aromatic heterocyclic compounds such as dibenzothiophene, dibenzofuran, dibenzoselenophene, furan, thiophene, benzofuran, benzothiophene, benzoselenophene, carbazole, indolocarbazole, pyridylindole, pyrrolodipyrindine, pyrazole, imidazole, triazole, oxazole, thiazole, oxadiazole, oxatriazole, dioxazole, thiadiazole, pyridine, pyridazine, pyrimidine, pyrazine, triazine, oxazine, oxathiazine, oxadiazine, indole, benzimidazole, indazole, indoxazine, benzoxazole, benzisoxazole, benzothiazole, quinoline, isoquinoline, cinnoline, quinazoline, quinoxaline, naphthyridine, phthalazine, pteridine, xanthene, acridine, phenazine, phenothiazine, phenoxazine, benzofuropyridine, furodipyrindine, benzothienopyridine, thienodipyrindine, benzoselenophenopyridine, and selenophenodipyrindine; and the group consisting of 2 to 10 cyclic structural units which are groups of the same type or different types selected from the aromatic hydrocarbon cyclic group and the aromatic heterocyclic group and are bonded to each other directly or via at least one of oxygen atom, nitrogen atom, sulfur atom, silicon atom, phosphorus atom, boron atom, chain structural unit and the aliphatic cyclic group. Wherein each Ar is further substituted by a substituent selected from the group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acids, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof.

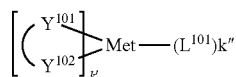
In one aspect,  $\text{Ar}^1$  to  $\text{Ar}^9$  is independently selected from the group consisting of:



wherein k is an integer from 1 to 20;  $\text{X}^{101}$  to  $\text{X}^{108}$  is C (including CH) or N;  $\text{Z}^{101}$  is  $\text{NAr}^1$ , O, or S;  $\text{Ar}^1$  has the same group defined above.

Examples of metal complexes used in HIL or HTL include, but are not limited to the following general formula:

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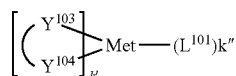


wherein Met is a metal, which can have an atomic weight greater than 40; ( $Y^{101}$ - $Y^{102}$ ) is a bidentate ligand,  $Y^{101}$  and  $Y^{102}$  are independently selected from C, N, O, P, and S;  $L^{101}$  is an ancillary ligand;  $k'$  is an integer value from 1 to the maximum number of ligands that may be attached to the metal; and  $k'+k''$  is the maximum number of ligands that may be attached to the metal.

In one aspect, ( $Y^{101}$ - $Y^{102}$ ) is a 2-phenylpyridine derivative. In another aspect, ( $Y^{101}$ - $Y^{102}$ ) is a carbene ligand. In a further aspect, Met is selected from Ir, Pt, Os, and Zn. In a further aspect, the metal complex has a smallest oxidation potential in solution vs.  $\text{Fc}^+/\text{Fc}$  couple less than about 0.6 V. Host:

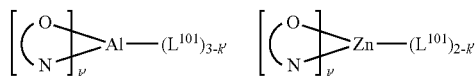
The light emitting layer of the organic EL device of the present invention preferably contains at least a metal complex as light emitting material, and may contain a host material using the metal complex as a dopant material. Examples of the host material are not particularly limited, and any metal complexes or organic compounds may be used as long as the triplet energy of the host is larger than that of the dopant. While the Table below categorizes host materials as preferred for devices that emit various colors, any host material may be used with any dopant so long as the triplet criteria is satisfied.

Examples of metal complexes used as host are preferred to have the following general formula:



wherein Met is a metal; ( $Y^{103}$ - $Y^{104}$ ) is a bidentate ligand,  $Y^{103}$  and  $Y^{104}$  are independently selected from C, N, O, P, and S;  $L^{101}$  is an another ligand;  $k'$  is an integer value from 1 to the maximum number of ligands that may be attached to the metal; and  $k'+k''$  is the maximum number of ligands that may be attached to the metal.

In one aspect, the metal complexes are:



wherein (O—N) is a bidentate ligand, having metal coordinated to atoms O and N.

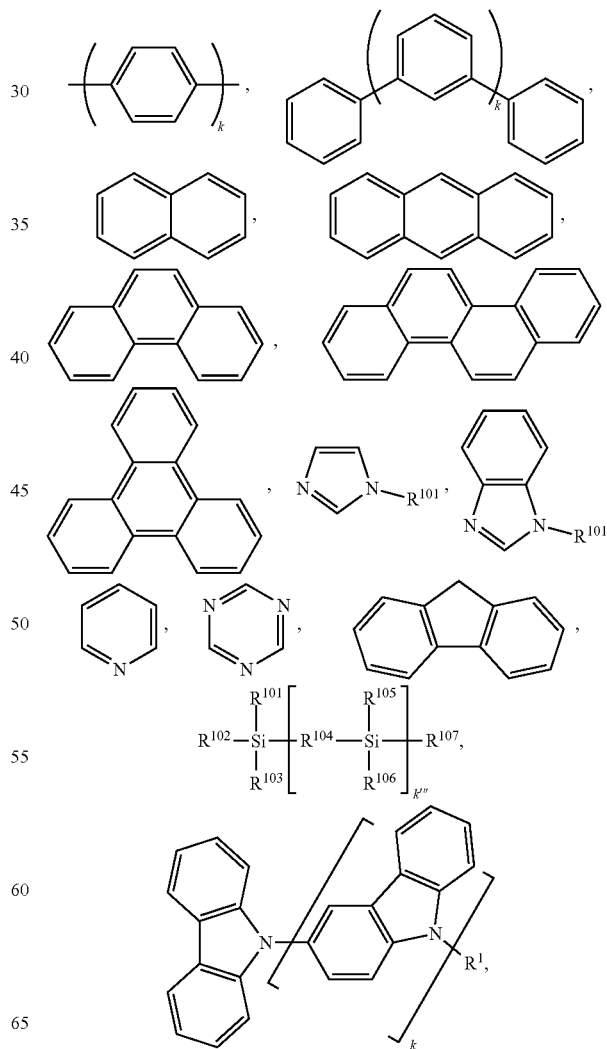
In another aspect, Met is selected from Ir and Pt. In a further aspect, ( $Y^{103}$ - $Y^{104}$ ) is a carbene ligand.

Examples of organic compounds used as host are selected from the group consisting of aromatic hydrocarbon cyclic compounds such as benzene, biphenyl, triphenyl, triphenylene, naphthalene, anthracene, phenalene, phenanthrene, fluorene, pyrene, chrysene, perylene, and azulene; the group consisting of aromatic heterocyclic compounds such as dibenzothiophene, dibenzofuran, dibenzoselenophene, furan, thiophene, benzofuran, benzothiophene, benzoselenophene, carbazole, indolocarbazole, pyridylindole, pyrrolodipyridine, pyrazole, imidazole, triazole, oxazole, thiazole, oxadiazole, oxatriazole, dioxazole, thiadiazole,

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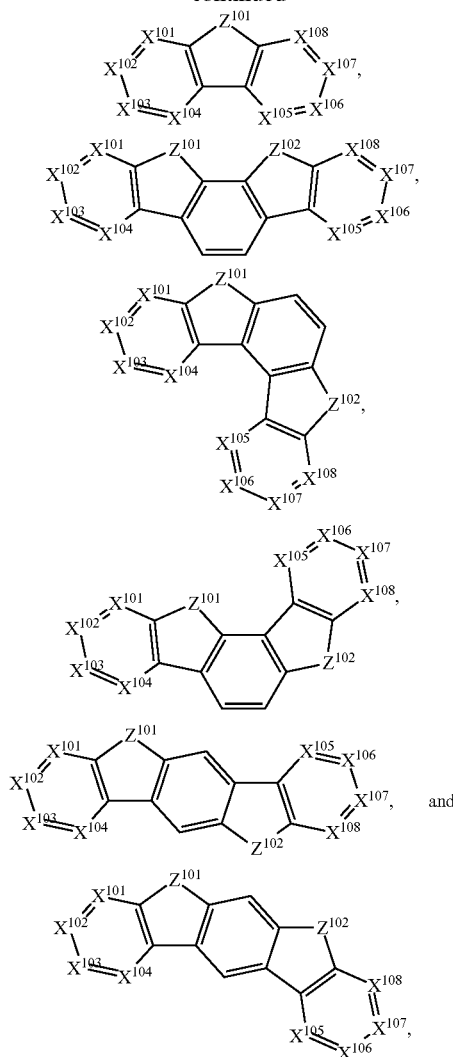
pyridine, pyridazine, pyrimidine, pyrazine, triazine, oxazine, oxathiazine, oxadiazine, indole, benzimidazole, indazole, indoxazine, benzoxazole, benzisoxazole, benzothiazole, quinoline, isoquinoline, cinnoline, quinazoline, quinoxaline, naphthyridine, phthalazine, pteridine, xanthene, acridine, phenazine, phenothiazine, phenoxazine, benzofuopyridine, furodipyridine, benzothienopyridine, thienodipyridine, benzoselenophenopyridine, and selenophenodipyridine; and the group consisting of 2 to 10 cyclic structural units which are groups of the same type or different types selected from the aromatic hydrocarbon cyclic group and the aromatic heterocyclic group and are bonded to each other directly or via at least one of oxygen atom, nitrogen atom, sulfur atom, silicon atom, phosphorus atom, boron atom, chain structural unit and the aliphatic cyclic group. Wherein each group is further substituted by a substituent selected from the group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acids, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof.

In one aspect, the host compound contains at least one of the following groups in the molecule:



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wherein R<sup>101</sup> to R<sup>107</sup> is independently selected from the group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acids, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof, when it is aryl or heteroaryl, it has the similar definition as Ar's mentioned above. k is an integer from 0 to 20 or 1 to 20; k''' is an integer from 0 to 20. X<sup>101</sup> to X<sup>108</sup> is selected from C (including CH) or N.

$Z^{101}$  and  $Z^{102}$  is selected from NR<sup>101</sup>, O, or S.

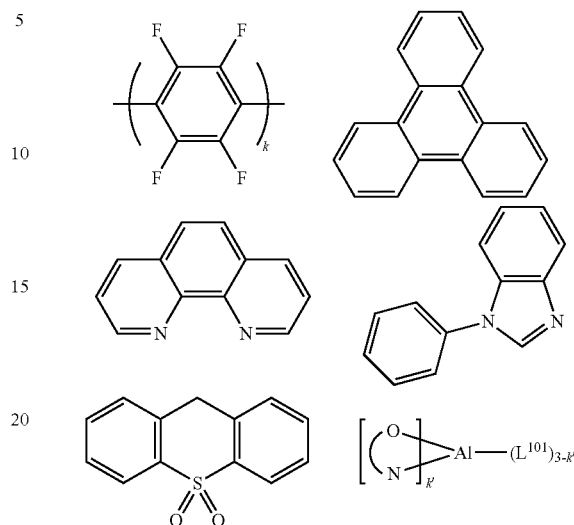
HBL:

A hole blocking layer (HBL) may be used to reduce the number of holes and/or excitons that leave the emissive layer. The presence of such a blocking layer in a device may result in substantially higher efficiencies as compared to a similar device lacking a blocking layer. Also, a blocking layer may be used to confine emission to a desired region of an OLED.

In one aspect, the compound used in the HBL contains the 65  
same molecule or the same functional groups used as the  
host described above.

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In another aspect, the compound used in the HBL contains at least one of the following groups in the molecule:

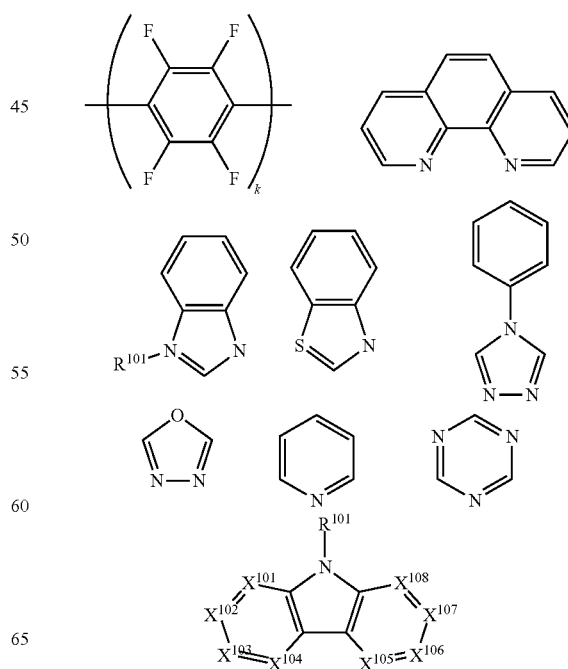


wherein k is an integer from 1 to 20;  $L^{101}$  is an another ligand, k' is an integer from 1 to 3.

ETL:

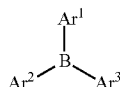
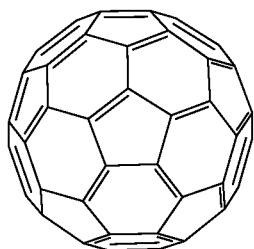
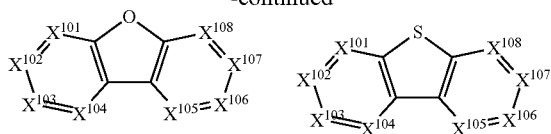
Electron transport layer (ETL) may include a material capable of transporting electrons. Electron transport layer may be intrinsic (undoped), or doped. Doping may be used to enhance conductivity. Examples of the ETL material are not particularly limited, and any metal complexes or organic compounds may be used as long as they are typically used to transport electrons.

In one aspect, the compound used in ETL contains at least one of the following groups in the molecule:



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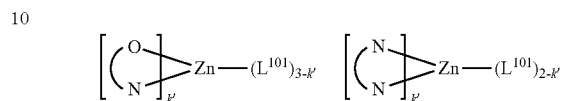
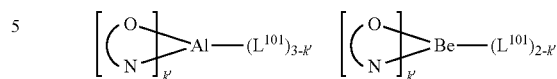
-continued



wherein  $R^{101}$  is selected from the group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acids, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof, when it is aryl or heteroaryl, it has the similar definition as  $Ar$ 's mentioned above.  $Ar^1$  to  $Ar^3$  has the similar definition as  $Ar$ 's mentioned above.  $k$  is an integer from 1 to 20.  $X^{101}$  to  $X^{108}$  is selected from C (including CH) or N.

66

In another aspect, the metal complexes used in ETL contains, but is not limited to, the following general formula:



15

wherein (O—N) or (N—N) is a bidentate ligand, having metal coordinated to atoms O, N or N, N;  $L^{101}$  is another ligand;  $k'$  is an integer value from 1 to the maximum number of ligands that may be attached to the metal.

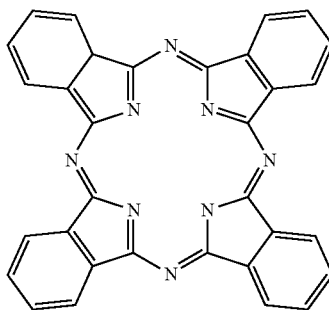
In any above-mentioned compounds used in each layer of the OLED device, the hydrogen atoms can be partially or fully deuterated. Thus, any specifically listed substituent, such as, without limitation, methyl, phenyl, pyridyl, etc. encompasses undeuterated, partially deuterated, and fully deuterated versions thereof. Similarly, classes of substituents such as, without limitation, alkyl, aryl, cycloalkyl, heteroaryl, etc. also encompass undeuterated, partially deuterated, and fully deuterated versions thereof.

In addition to and/or in combination with the materials disclosed herein, many hole injection materials, hole transporting materials, host materials, dopant materials, exciton/hole blocking layer materials, electron transporting and electron injecting materials may be used in an OLED. Non-limiting examples of the materials that may be used in an OLED in combination with materials disclosed herein are listed in Table A below. Table A lists non-limiting classes of materials, non-limiting examples of compounds for each class, and references that disclose the materials.

TABLE A

MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Hole injection materials		

Phthalocyanine and porphyrin compounds



Appl. Phys. Lett. 69, 2160 (1996)

TABLE A-continued

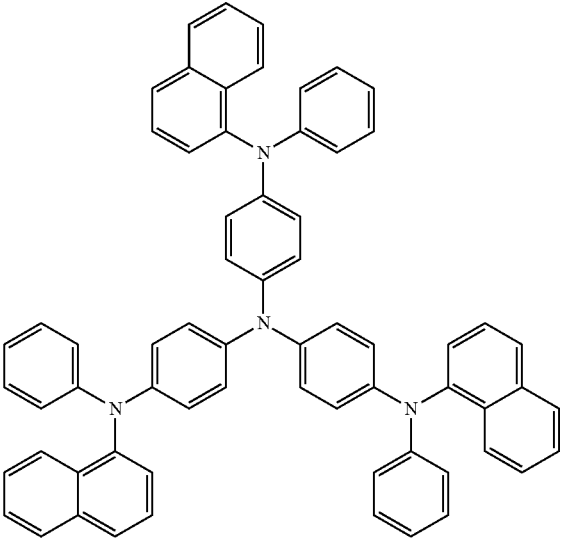
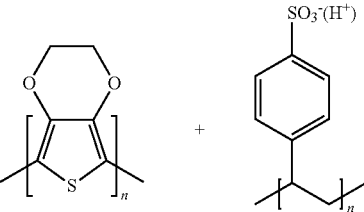
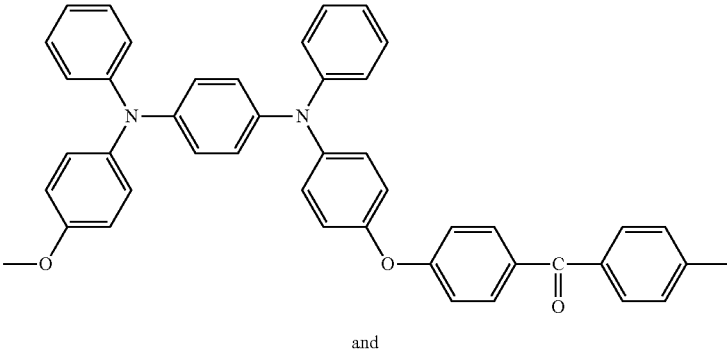
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Starburst triarylaminines		J. Lumin. 72-74, 985 (1997)
CF <sub>x</sub> Fluorohydrocarbon polymer	$\text{---}[\text{CH}_x\text{F}_y]_n\text{---}$	Appl. Phys. Lett. 78, 673 (2001)
Conducting polymers (e.g., PEDOT:PSS, polyaniline, polythiophene)		Synth. Met. 87, 171 (1997) WO2007002683
Phosphonic acid and silane SAMs	$\text{N} \left( \text{C}_6\text{H}_4\text{---SiCl}_2 \right)_3$	U.S. 20030162053
Triarylamine or polythiophene polymers with conductivity dopants	 <p style="text-align: center;">and</p>	EP1725079A1



TABLE A-continued

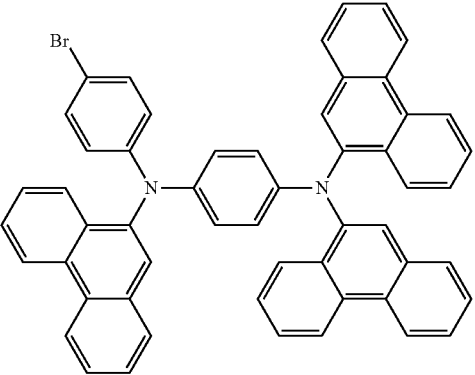
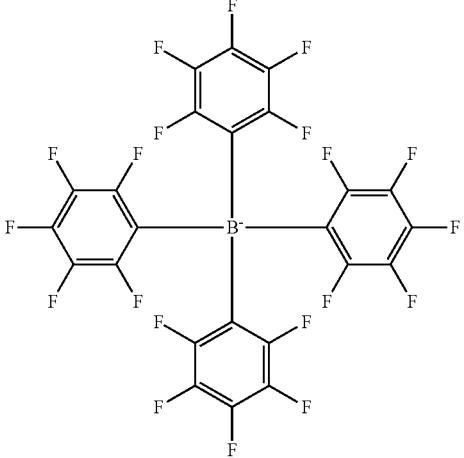
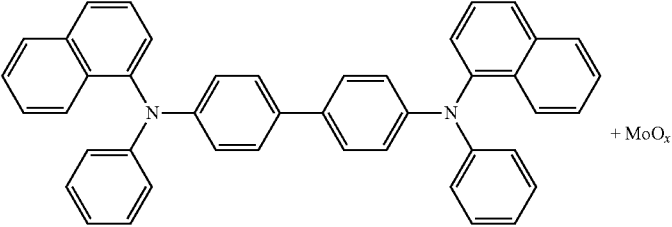
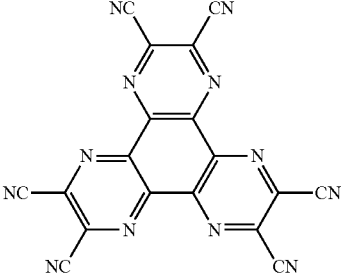
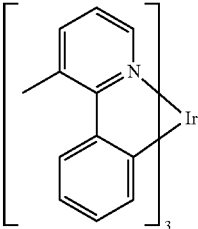
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Organic compounds with conductive inorganic compounds, such as molybdenum and tungsten oxides	  	U.S. 20050123751 SID Symposium Digest, 37, 923 (2006) WO2009018009
n-type semiconducting organic complexes		U.S. 20020158242
Metal organometallic complexes		U.S. 20060240279

TABLE A-continued

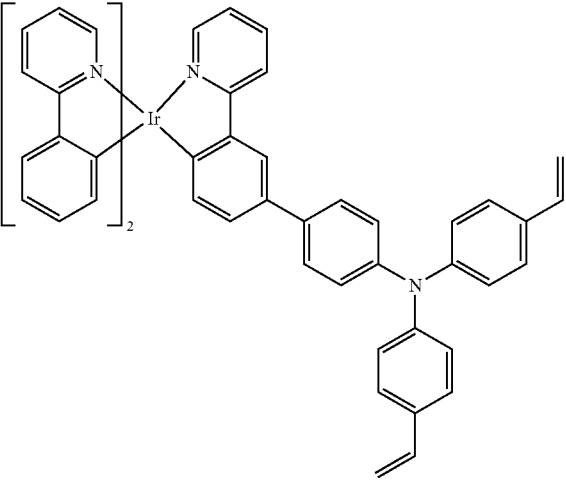
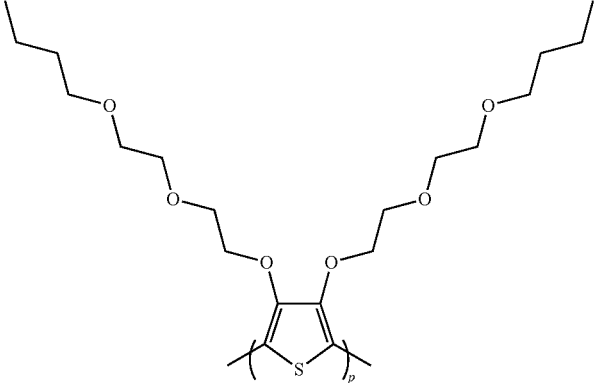
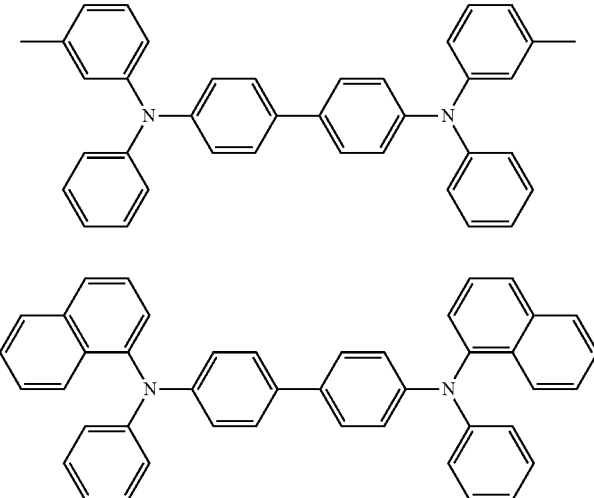
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Cross-linkable compounds		U.S. 20080220265
Polythiophene based polymers and copolymers		WO 2011075644 EP2350216
Hole transporting materials		
Triarylamines (e.g., TPD, $\alpha$ -NPD)		Appl. Phys. Lett. 51, 913 (1987)  U.S. Pat. No. 5,061,569

TABLE A-continued

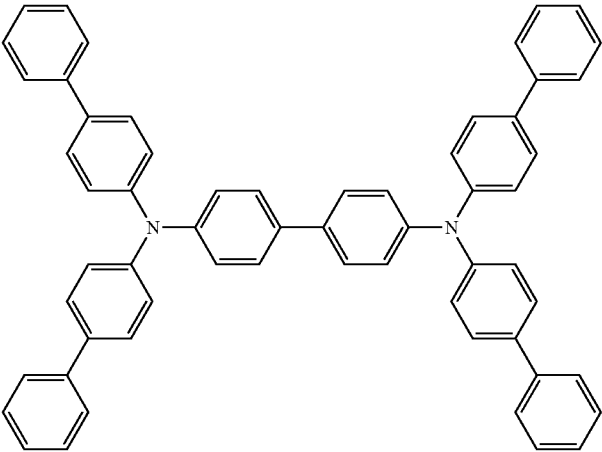
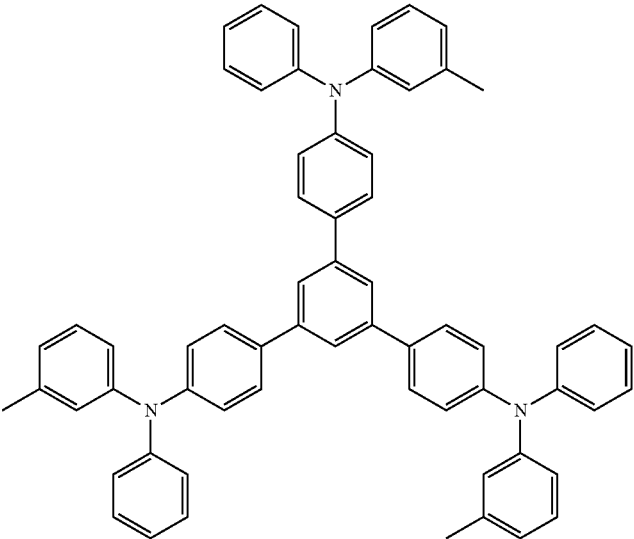
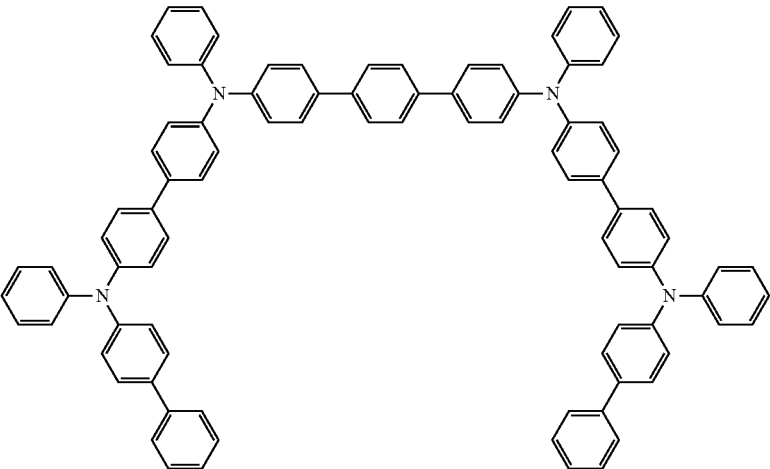
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		EP650955
		J. Mater. Chem. 3, 319 (1993)
		Appl. Phys. Lett. 90, 183503 (2007)

TABLE A-continued

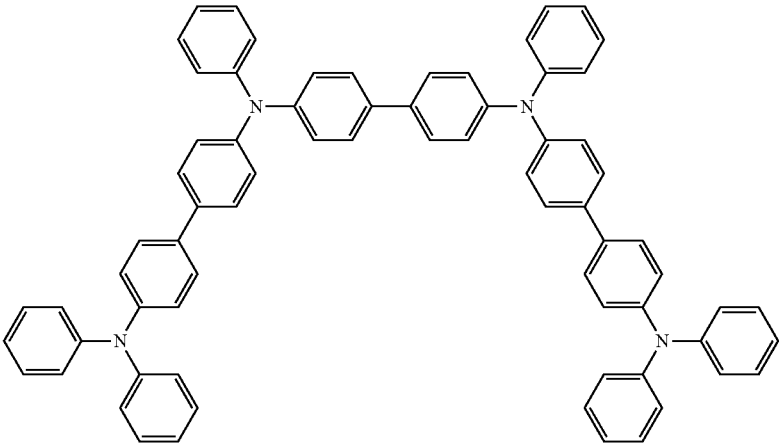
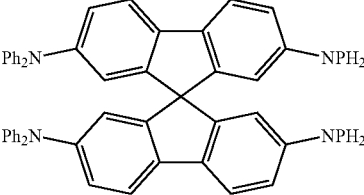
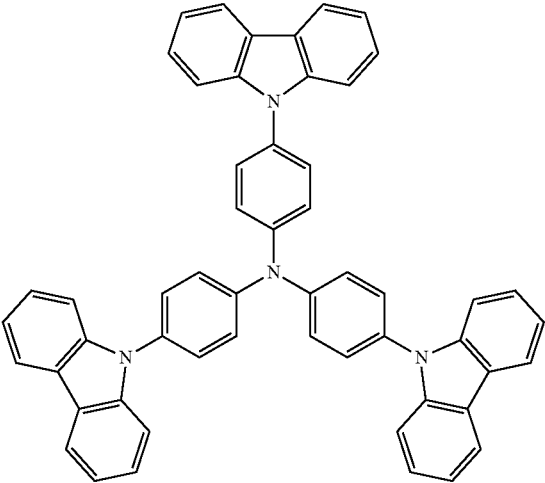
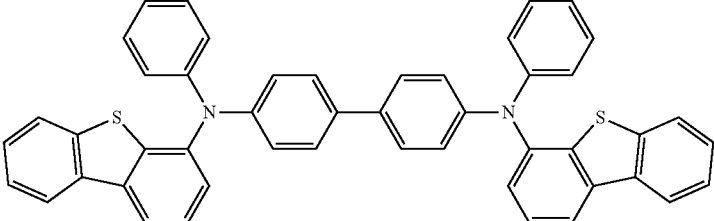
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Triarylamine on spirofluorene core		Appl. Phys. Lett. 90, 183503 (2007)
Arylamine carbazole compounds		Synth. Met. 91, 209 (1997)
Arylamine carbazole compounds		Adv. Mater. 6, 677 (1994), U.S. 20080124572
Triarylamine with (di)benzothiophene/ (di)benzofuran		U.S. 20070278938, U.S. 20080106190 U.S. 20110163302

TABLE A-continued

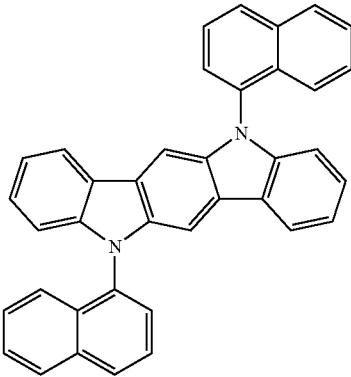
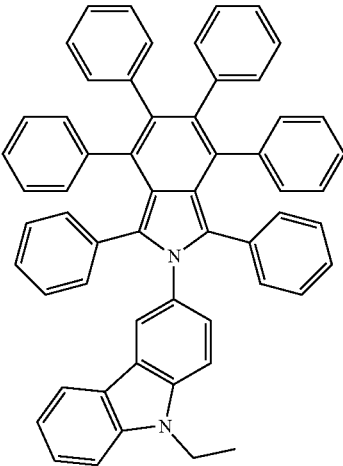
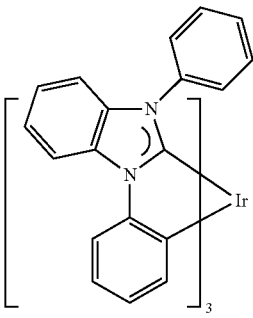
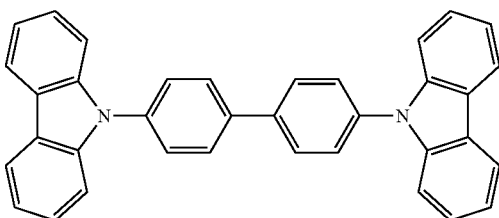
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Indolocarbazoles		Synth. Met. 111, 421 (2000)
Isoindole compounds		Chem. Mater. 15, 3148 (2003)
Metal carbene complexes		U.S. 20080018221
Phosphorescent OLED host materials Red hosts		
Arylcarbazoles		Appl. Phys. Lett. 78, 1622 (2001)

TABLE A-continued

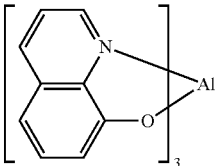
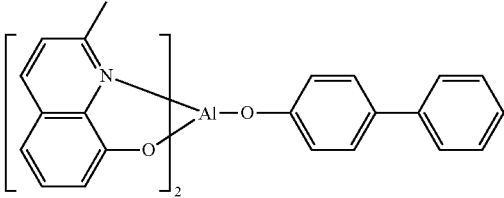
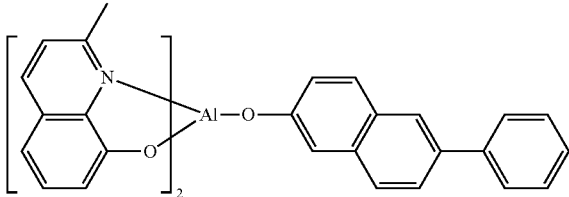
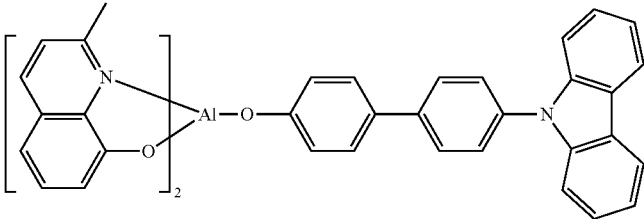
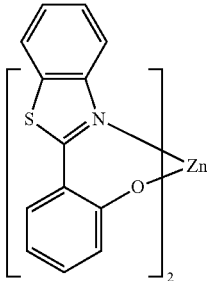
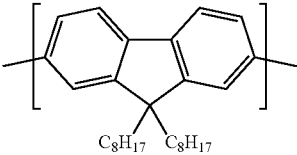
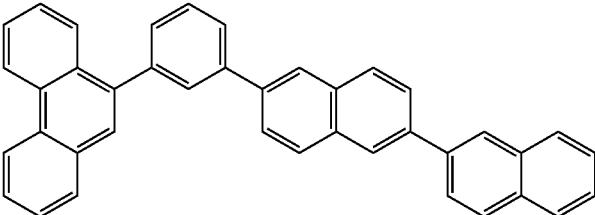
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Metal 8-hydroxyquinolates (e.g., Alq <sub>3</sub> , BAlq)		Nature 395, 151 (1998)
		U.S. 20060202194
		WO2005014551
		WO2006072002
Metal phenoxybenzothiazole compounds		Appl. Phys. Lett. 90, 123509 (2007)
Conjugated oligomers and polymers (e.g., polyfluorene)		Org. Electron. 1, 15 (2000)
Aromatic fused rings		WO2009066779, WO2009066778, WO2009063833, U.S. 20090045731, U.S. 20090045730, WO2009008311, U.S. 20090008605, U.S. 20090009065

TABLE A-continued

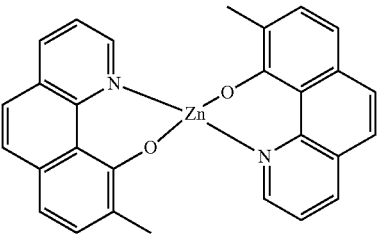
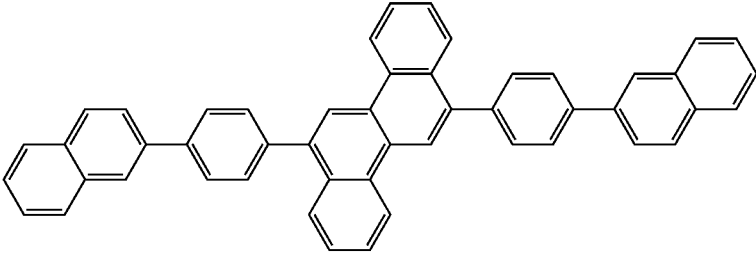
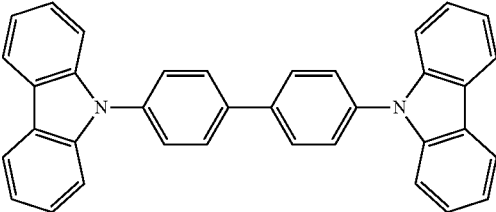
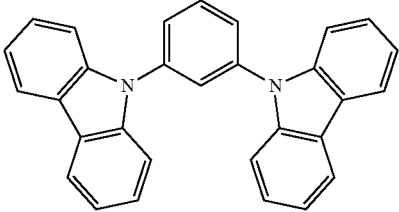
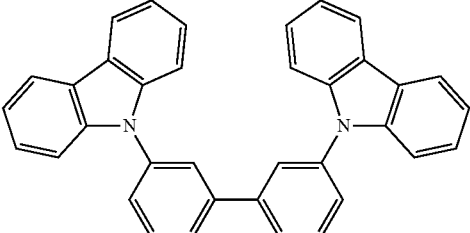
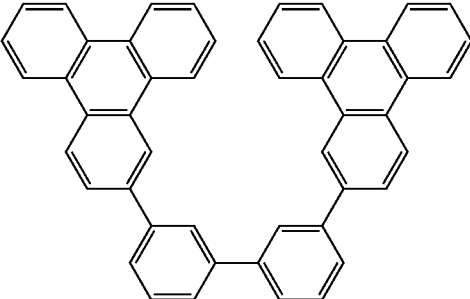
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Zinc complexes		WO2010056066
Chrysene based compounds		WO2011086863
Green hosts		
Arylcarbazoles		Appl. Phys. Lett. 78, 1622 (2001)
		U.S. 20030175553
		WO2001039234
Aryltriphenylene compounds		U.S. 20060280965

TABLE A-continued

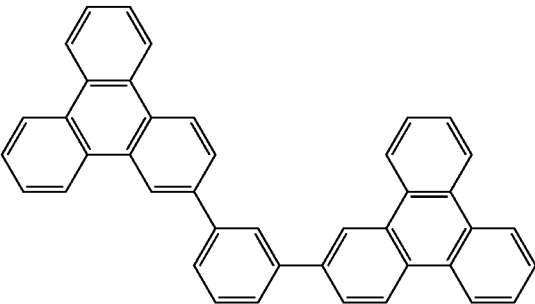
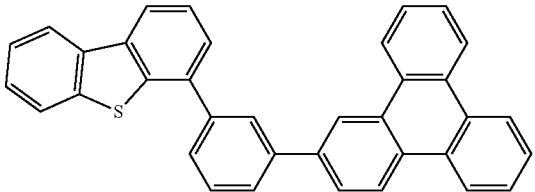
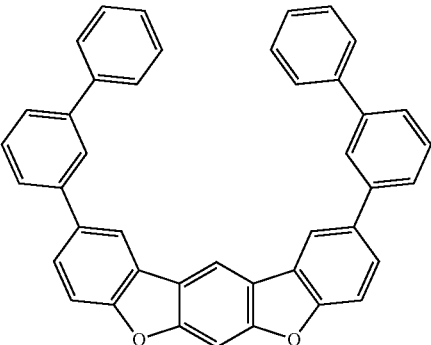
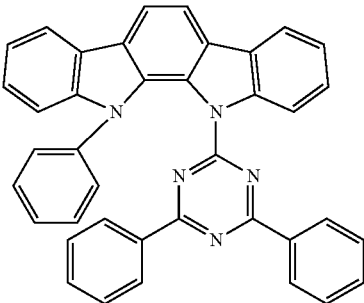
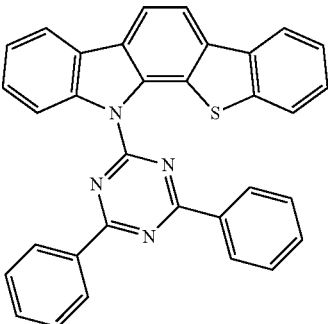
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Poly-fused heteroaryl compounds		U.S. 20060280965
		WO2009021126
		U.S. 20090309488 U.S. 20090302743 U.S. 20100012931
Donor acceptor type molecules		WO2008056746
		WO2010107244



TABLE A-continued

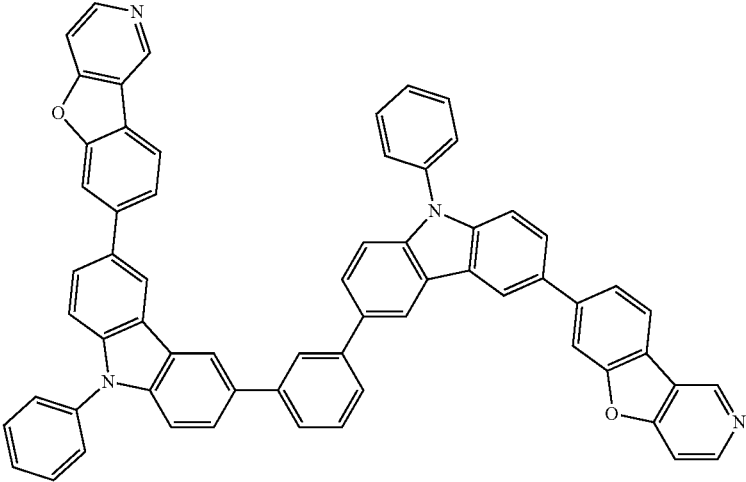
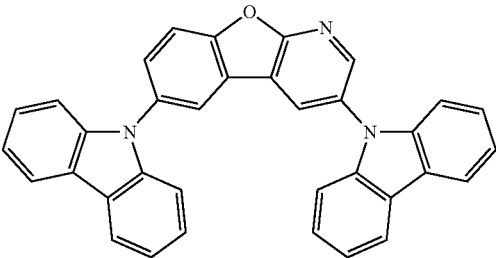
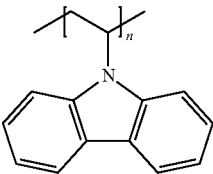
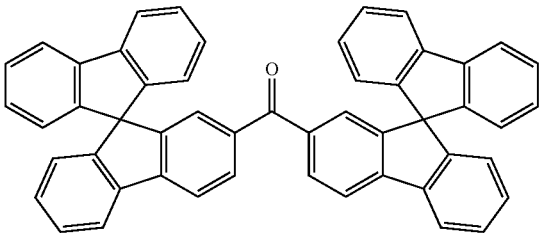
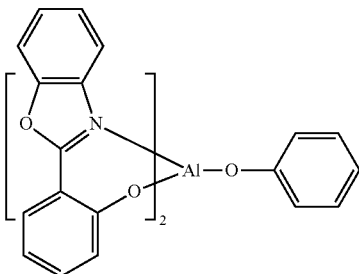
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Aza-carbazole/ DBT/DBF		JP2008074939
		U.S. 20100187984
Polymers (e.g., PVK)		Appl. Phys. Lett. 77, 2280 (2000)
Spirofluorene compounds		WO2004093207
Metal phenoxybenzoxazole compounds		WO2005089025

TABLE A-continued

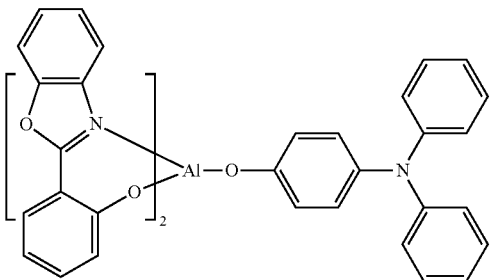
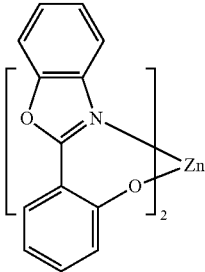
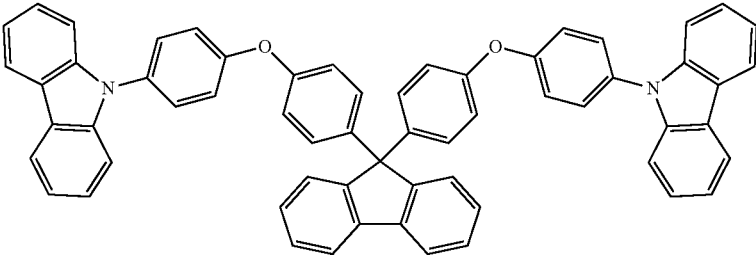
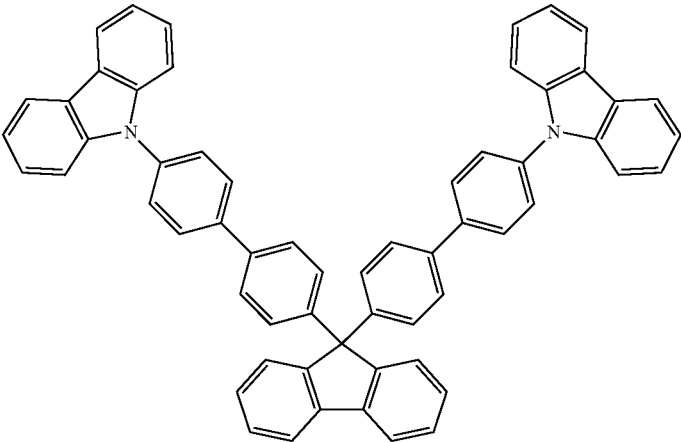
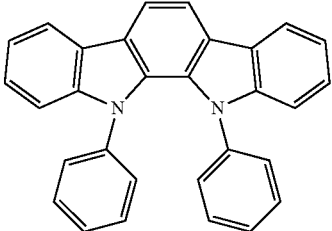
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		WO2006132173
		JP200511610
Spirofluorene-carbazole compounds		JP2007254297
		JP2007254297
Indolocarbazoles		WO2007063796

TABLE A-continued

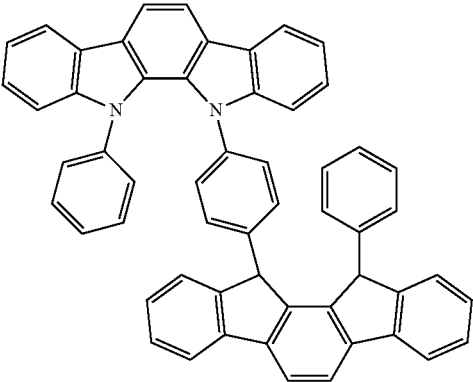
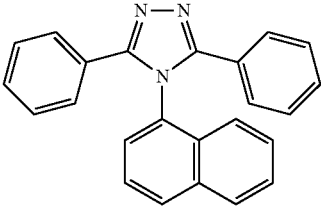
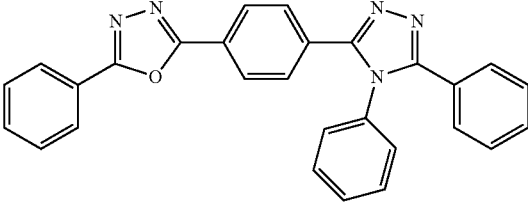
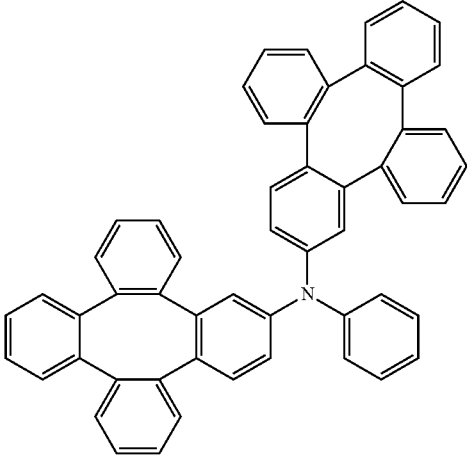
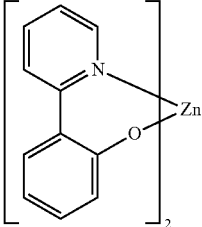
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
5-member ring electron deficient heterocycles (e.g., triazole, oxadiazole)		WO2007063754
		J. Appl. Phys. 90, 5048 (2001)
Tetraphenylene complexes		WO2004107822
		U.S. 20050112407
Metal phenoxypyridine compounds		WO2005030900

TABLE A-continued

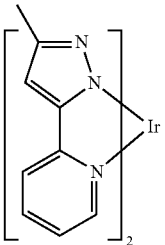
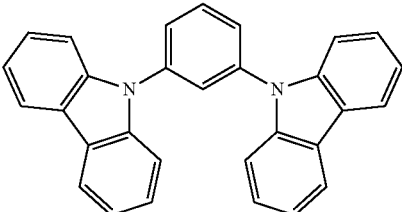
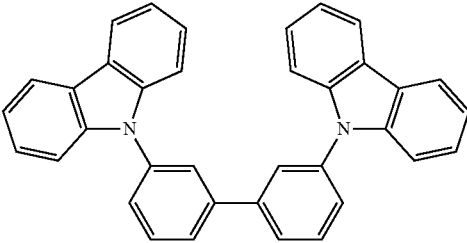
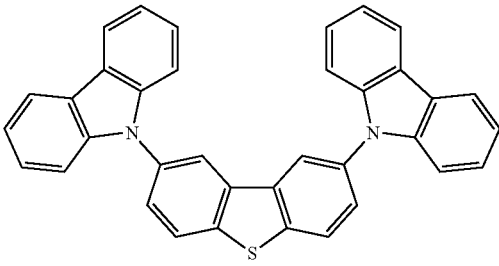
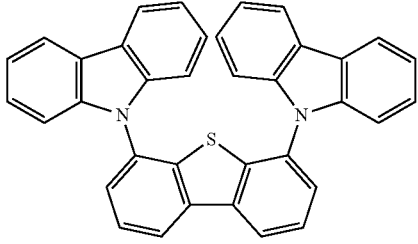
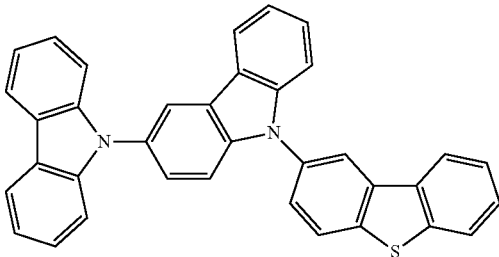
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Metal coordination complexes (e.g., Zn, Al with N <sup>-</sup> N ligands)		U.S. 20040137268, U.S. 20040137267
Blue hosts		
Arylcarbazoles		Appl. Phys. Lett, 82, 2422 (2003)
		U.S. 20070190359
Dibenzothiophene/ Dibenzofuran- carbazole compounds		WO2006114966, U.S. 20090167162
		U.S. 20090167162
		WO2009086028

TABLE A-continued

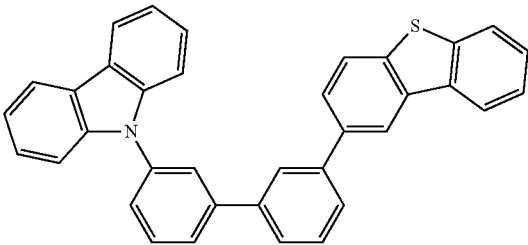
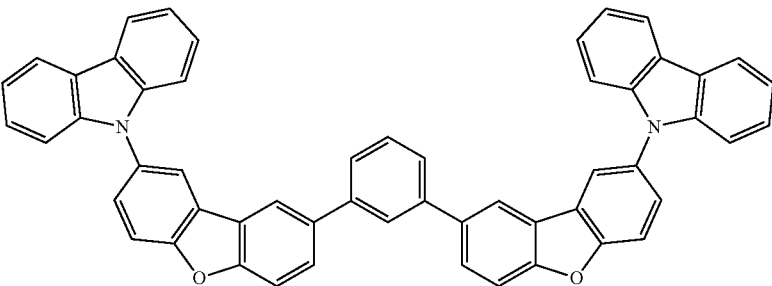
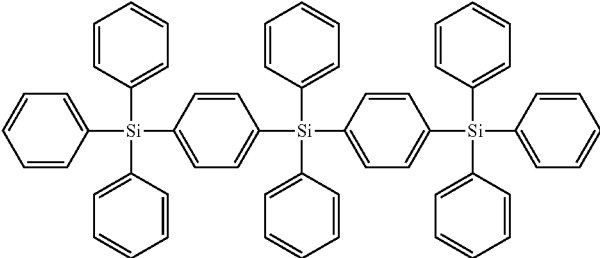
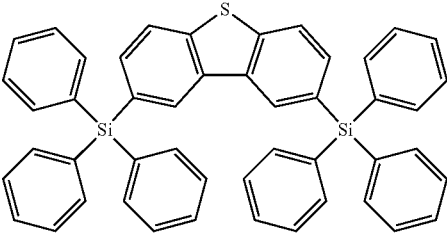
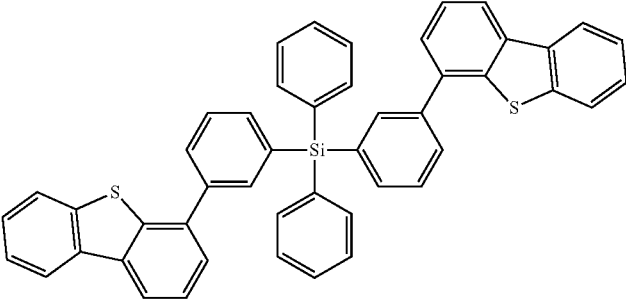
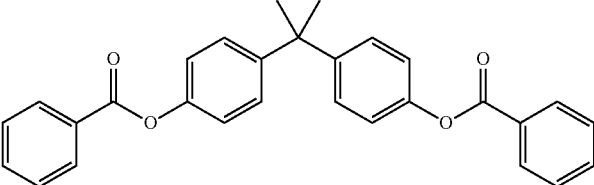
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		U.S. 20090030202, U.S. 20090017330
		U.S. 20100084966
Silicon aryl compounds		U.S. 20050238919
		WO2009003898
Silicon/ Germanium aryl compounds		EP2034538A
Aryl benzoyl ester		WO2006100298

TABLE A-continued

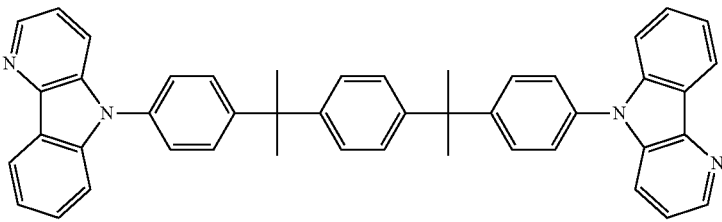
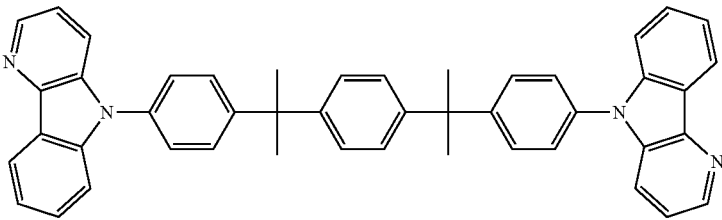
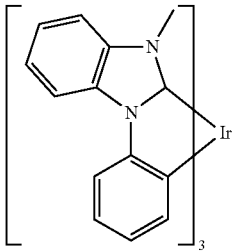
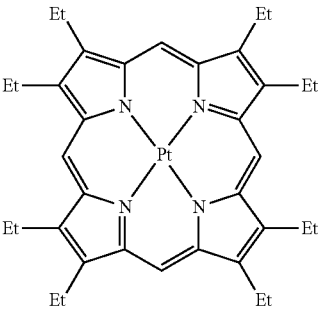
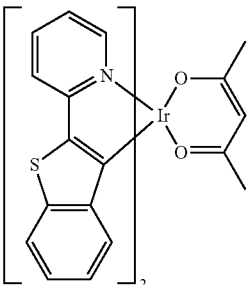
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Carbazole linked by non-conjugated groups		U.S. 20040115476
Aza-carbazoles		U.S. 20060121308
High triplet metal organometallic complex		U.S. 7,154,114
Phosphorescent dopants Red dopants		
Heavy metal porphyrins (e.g., PtOEP)		Nature 395, 151 (1998)
Iridium(III) organometallic complexes		Appl. Phys. Lett. 78, 1622 (2001)

TABLE A-continued

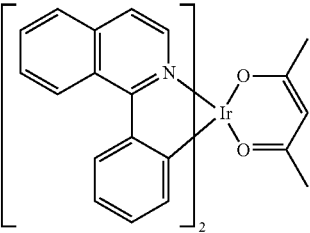
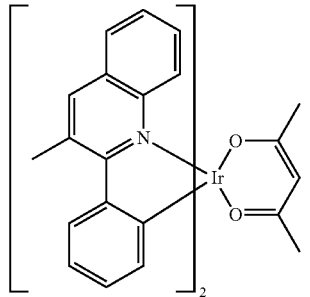
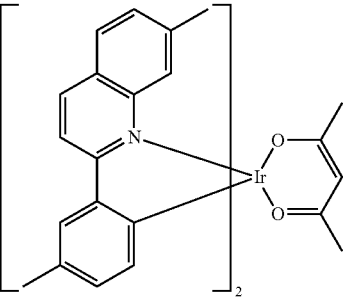
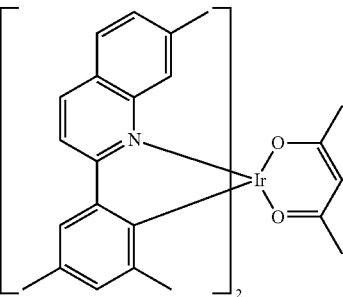
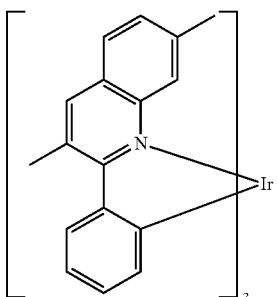
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
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		U.S. 20060202194
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		U.S. 20070087321

TABLE A-continued

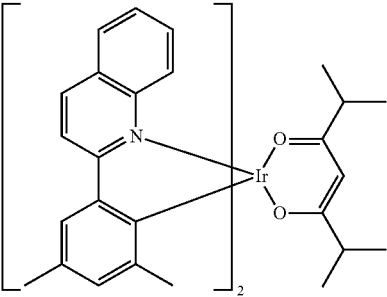
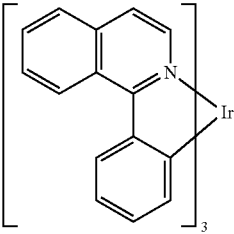
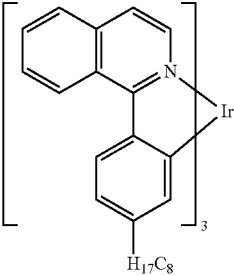
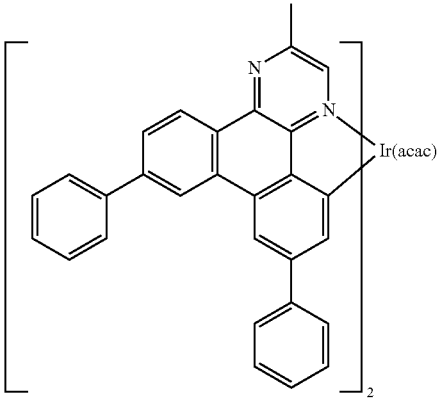
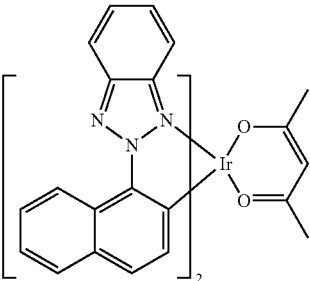
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		U.S. 20080261076 U.S. 20100090591
		U.S. 20070087321
		Adv. Mater. 19, 739 (2007)
		WO2009100991
		WO2008101842



TABLE A-continued

MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Platinum(II) organometallic complexes		U.S. Pat. No. 7,232,618
		WO2003040257
		U.S. 20070103060
Osmium(III) complexes		Chem. Mater. 17, 3532 (2005)
Ruthenium(II) complexes		Adv. Mater. 17, 1059 (2005)
Rhenium (I), (II), and (III) complexes		U.S. 20050244673

TABLE A-continued

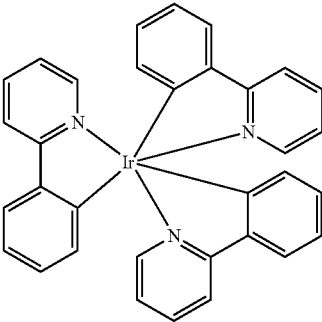
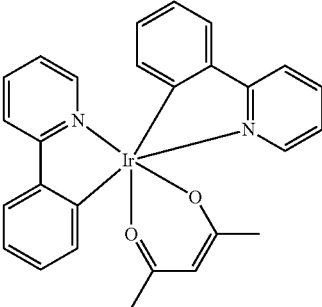
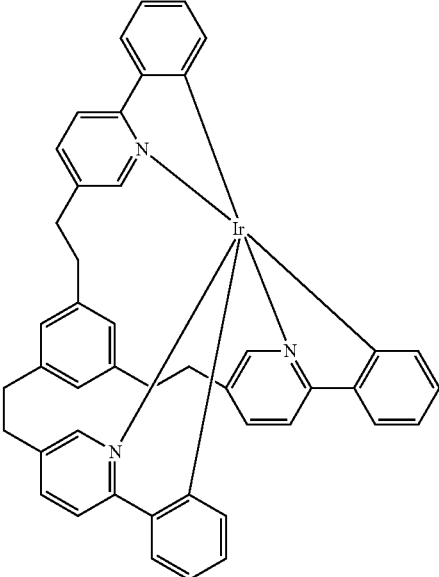
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Green dopants		
Iridium(III) organometallic complexes	 <p>The structure shows an Iridium(III) center coordinated to three 2,2'-bipyridine ligands in an octahedral geometry. Each bipyridine ligand consists of two benzene rings connected by a single bond, with nitrogen atoms at the 2 and 2' positions.</p>	Inorg. Chem. 40, 1704 (2001)
	and its derivatives	
	 <p>The structure shows an Iridium(III) center coordinated to two 2,2'-bipyridine ligands and one 2,6-dimethylphenolate ligand. The phenolate ligand is a benzene ring with two methyl groups at the 2 and 6 positions and an oxygen atom at the 1 position, which is coordinated to the Iridium center.</p>	
	 <p>The structure shows an Iridium(III) center coordinated to three bipyridine ligands. One of the bipyridine ligands has a long alkyl chain (hexyl group) attached to one of the benzene rings. The other two bipyridine ligands are unsubstituted.</p>	U.S. Pat. No. 7,332,232

TABLE A-continued

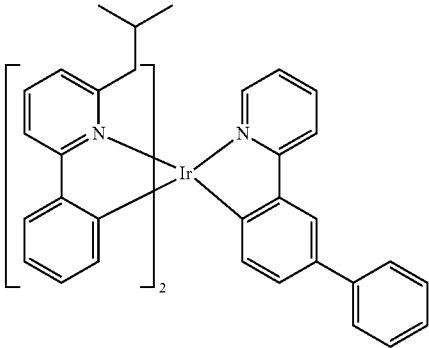
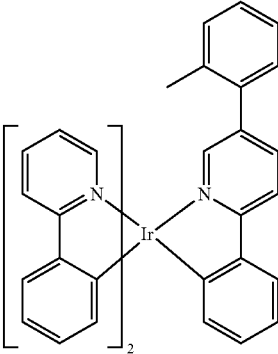
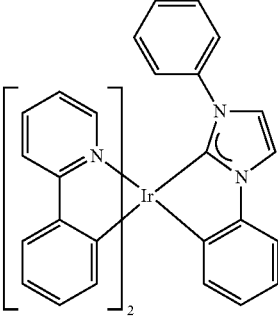
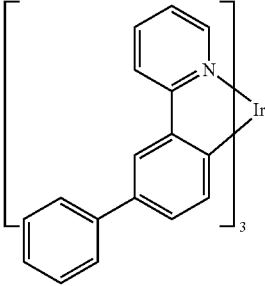
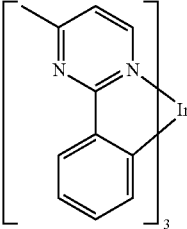
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
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		WO2010028151
		EP1841834B
		U.S. 20060127696
		U.S. 20090039776

TABLE A-continued

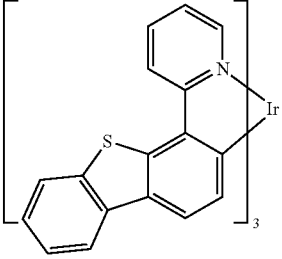
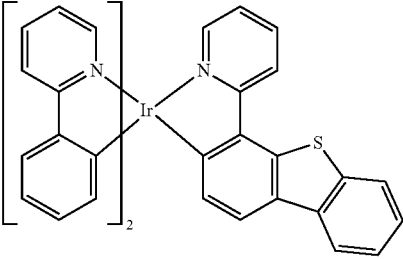
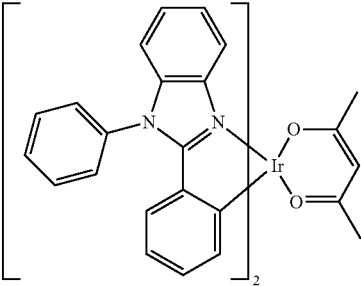
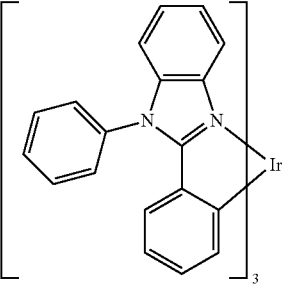
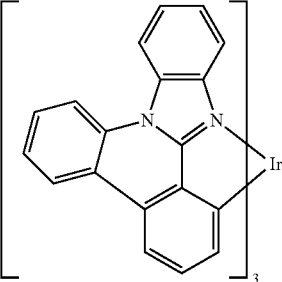
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		U.S. Pat. No. 6,921,915
		U.S. 20100244004
		U.S. Pat. No. 6,687,266
		Chem. Mater. 16, 2480 (2004)
		U.S. 20070190359

TABLE A-continued

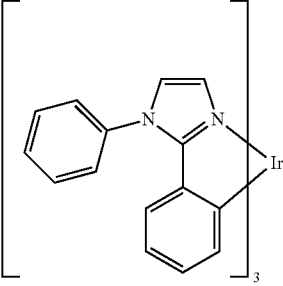
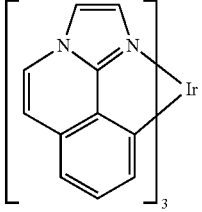
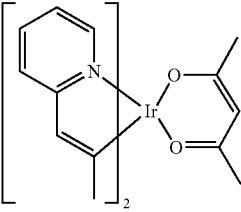
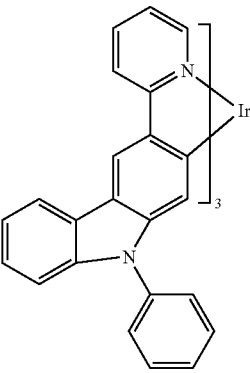
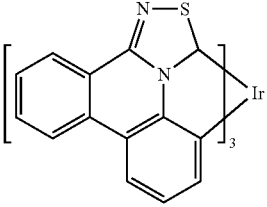
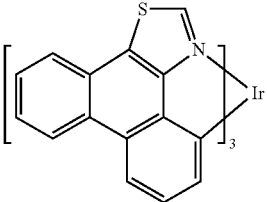
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		U.S. 20060008670 JP2007123392
		WO2010086089, WO2011044988
		Adv. Mater. 16, 2003 (2004)
		Angew. Chem. Int. Ed. 2006, 45, 7800
		WO2009050290
		U.S. 20090165846

TABLE A-continued

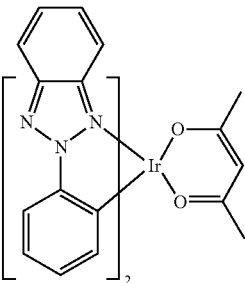
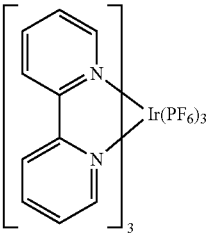
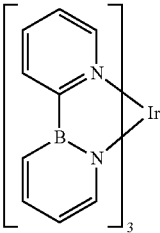
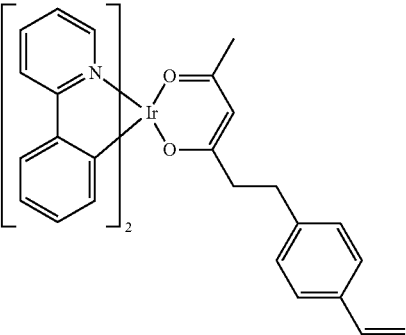
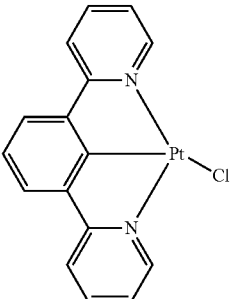
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		U.S. 20080015355
		U.S. 20010015432
		U.S. 20100295032
Monomer for polymeric metal organometallic compounds		U.S. Pat. No. 7,250,226, U.S. Pat. No. 7,396,598
Pt(II) organometallic complexes, including polydentate ligands		Appl. Phys. Lett. 86, 153505 (2005)

TABLE A-continued

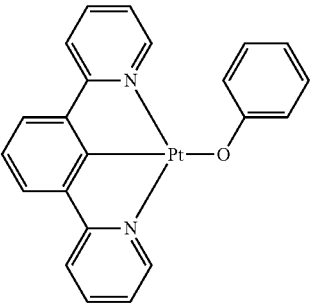
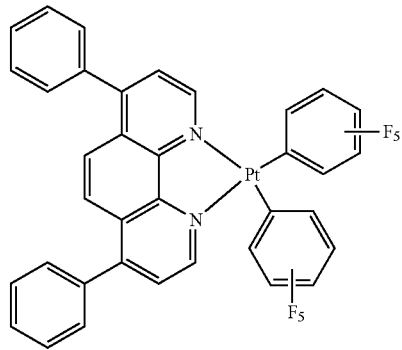
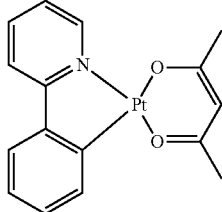
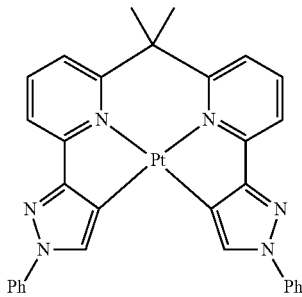
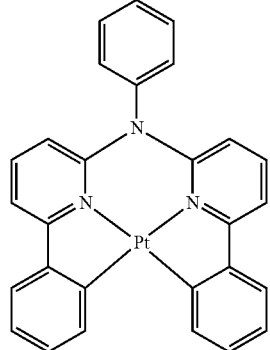
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		Chem. Lett. 34, 592 (2005)
		WO2002015645
		U.S. 20060263635
		U.S. 20060182992 U.S. 20070103060

TABLE A-continued

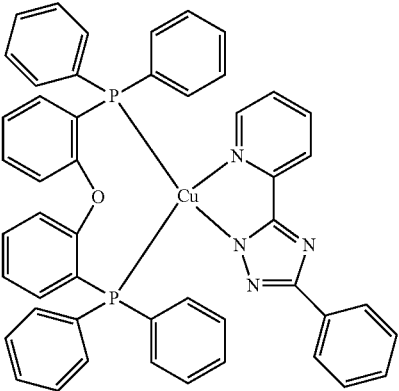
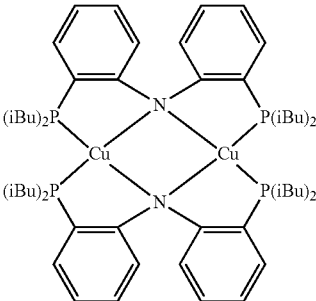
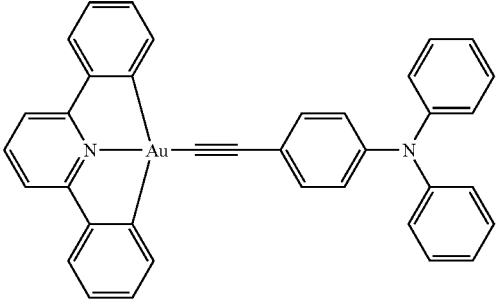
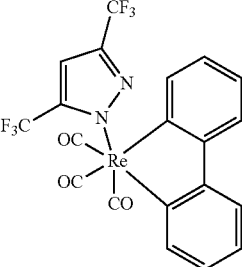
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Cu complexes		WO2009000673
		U.S. 20070111026
Gold complexes		Chem. Commun. 2906 (2005)
Rhenium(III) complexes		Inorg. Chem. 42, 1248 (2003)



TABLE A-continued

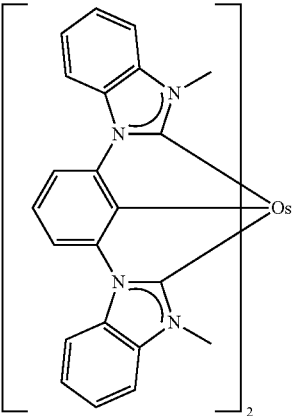
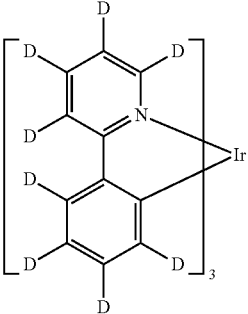
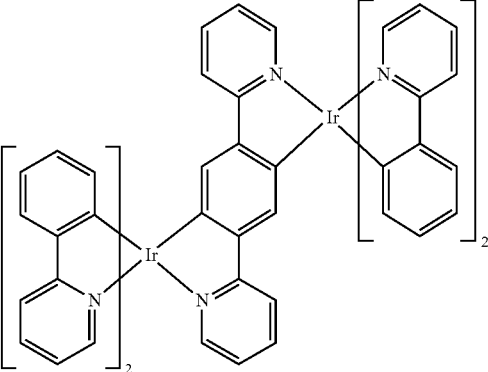
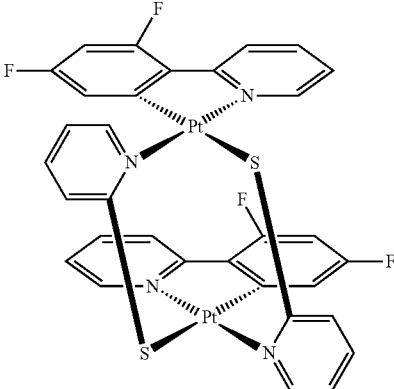
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Osmium(II) complexes		U.S. Pat. No. 7,279,704
Deuterated organometallic complexes		U.S. 20030138657
Organometallic complexes with two or more metal centers		U.S. 20030152802
		U.S. Pat. No. 7,090,928

TABLE A-continued

MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Blue dopants		
Iridium(III) organometallic complexes		WO2002002714
		WO2006009024
		U.S. 20060251923 U.S. 20110057559 U.S. 20110204333
		U.S. Pat. No. 7,393,599, WO2006056418, U.S. 20050260441, WO2005019373
		U.S. Pat. No. 7,534,505
		WO2011051404

TABLE A-continued

MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		U.S. Pat. No. 7,445,855
		U.S. 20070190359, U.S. 20080297033 U.S. 20100148663
		U.S. Pat. No. 7,338,722
		U.S. 20020134984
		Angew. Chem. Int. Ed. 47, 4542 (2008)

TABLE A-continued

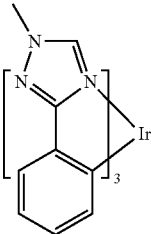
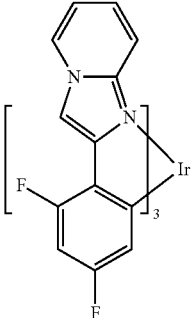
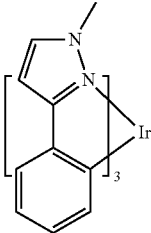
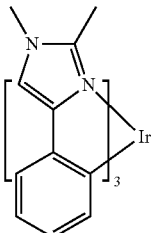
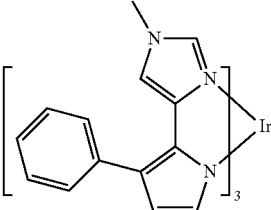
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		Chem. Mater. 18, 5119 (2006)
		Inorg. Chem. 46, 4308 (2007)
		WO2005123873
		WO2005123873
		WO2007004380

TABLE A-continued

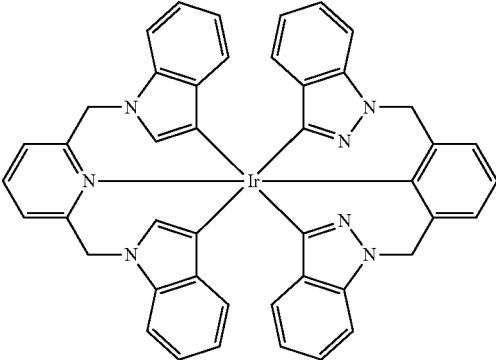
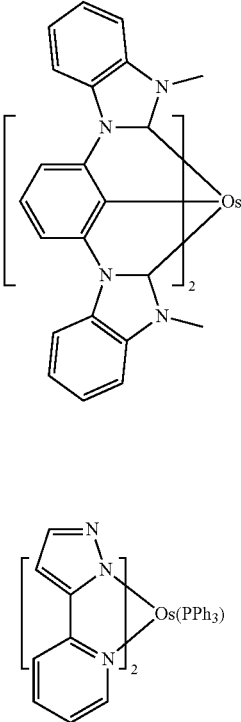
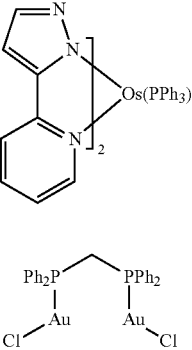
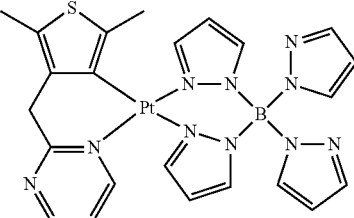
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Osmium(II) complexes		WO2006082742
Gold complexes		U.S. Pat. No. 7,279,704
Platinum(II) complexes		Organometallics 23, 3745 (2004)
		WO2006098120, WO2006103874

TABLE A-continued

MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Pt tetradentate complexes with at least one metal-carbene bond		U.S. Pat. No. 7,655,323
Exciton/hole blocking layer materials		
Bathocuprine compounds (e.g., BCP, BPhen)		Appl. Phys. Lett. 75, 4 (1999)
		Appl. Phys. Lett. 79, 449 (2001)
Metal 8-hydroxyquinolates (e.g., BALq)		Appl. Phys. Lett. 81, 162 (2002)
5-member ring electron deficient heterocycles such as triazole, oxadiazole, imidazole, benzoimidazole		Appl. Phys. Lett. 81, 162 (2002)

TABLE A-continued

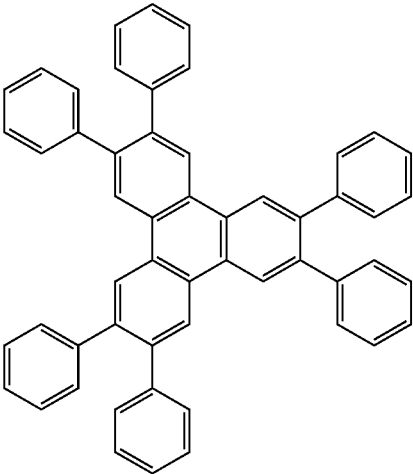
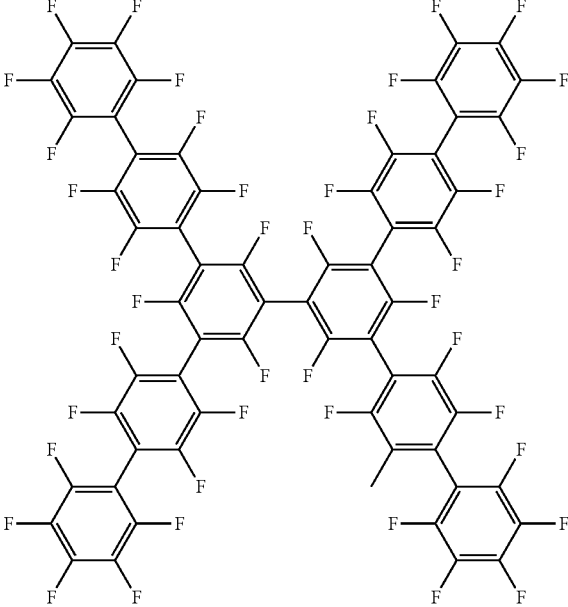
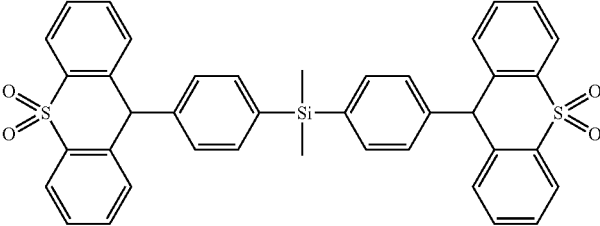
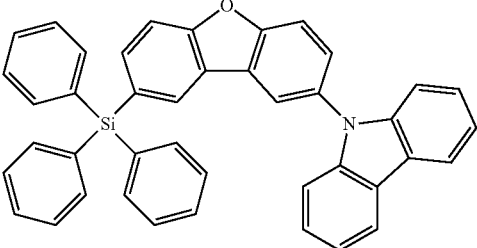
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Triphenylene compounds		U.S. 20050025993
Fluorinated aromatic compounds		Appl. Phys. Lett. 79, 156 (2001)
Phenothiazine-S-oxide		WO2008132085
Silylated five-membered nitrogen, oxygen, sulfur or phosphorus dibenzoheterocycles		WO2010079051

TABLE A-continued

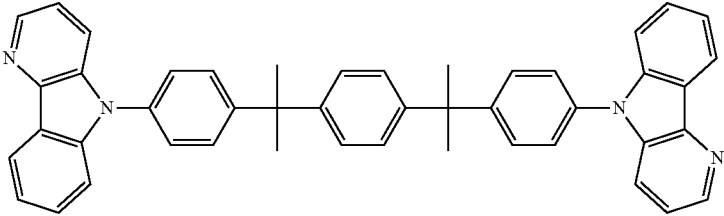
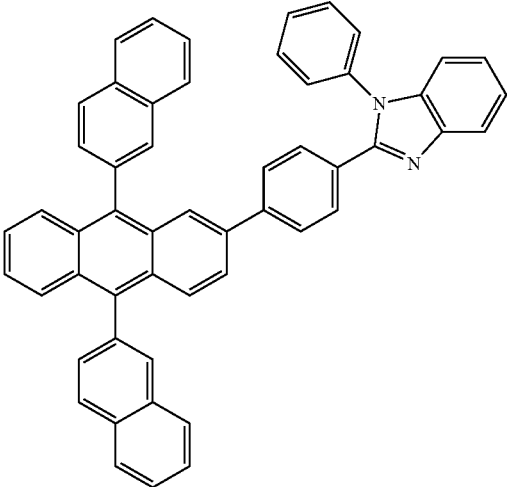
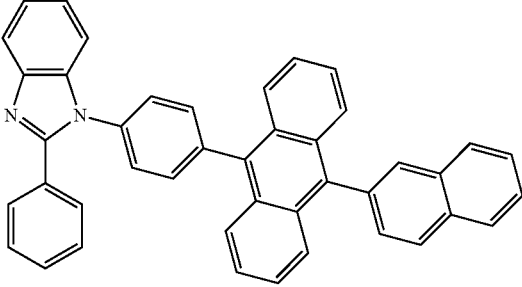
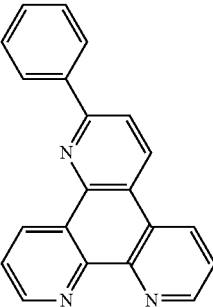
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Aza-carbazoles		U.S. 20060121308
Electron transporting materials		
Anthracene-benzimidazole compounds		WO2003060956
Aza triphenylene derivatives		U.S. 20090179554
		U.S. 20090115316



TABLE A-continued

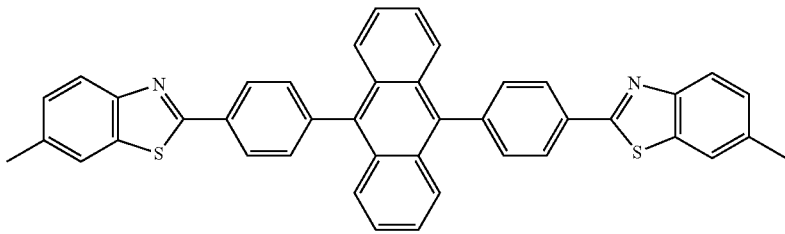
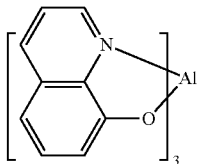
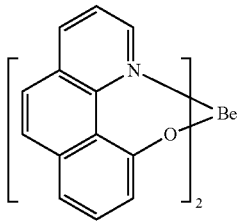
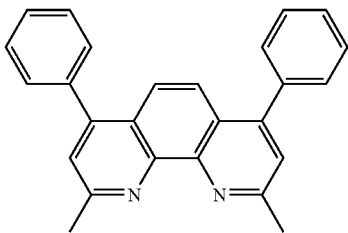
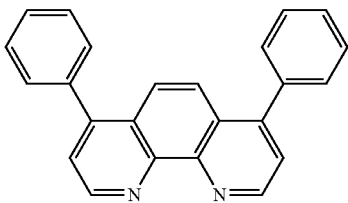
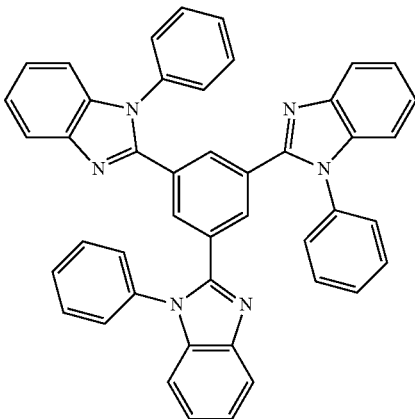
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Anthracene-enzothiazole compounds		Appl. Phys. Lett. 89, 063504 (2006)
Metal 8-hydroxyquinolates (e.g., Alq <sub>3</sub> , Zr <sub>q</sub> <sub>4</sub> )		Appl. Phys. Lett. 51, 913 (1987) U.S. Pat. No. 7,230,107
Metal hydroxy- benzoquinolates		Chem. Lett. 5, 905 (1993)
Bathocuprine compounds such as BCP, BPhen, etc		Appl. Phys. Lett. 91, 263503 (2007)
		Appl. Phys. Lett. 79, 449 (2001)
5-member ring electron deficient heterocycles (e.g., triazole, oxadiazole, imidazole, benzimidazole)		Appl. Phys. Lett. 74, 865 (1999)

TABLE A-continued

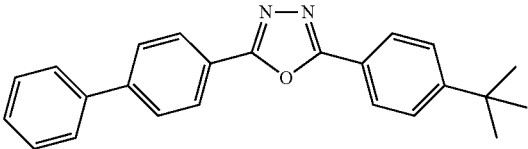
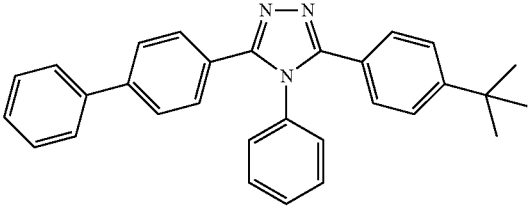
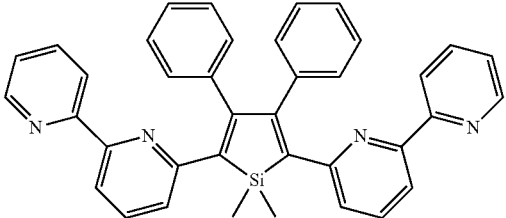
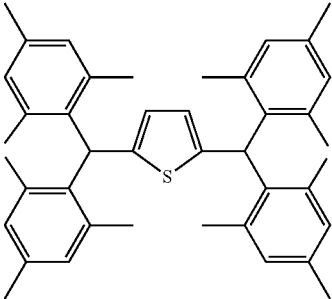
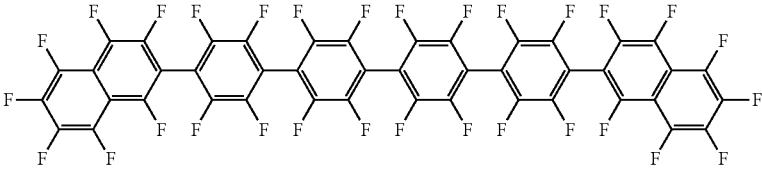
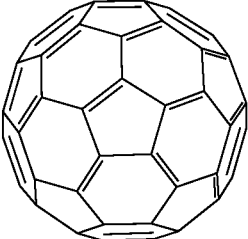
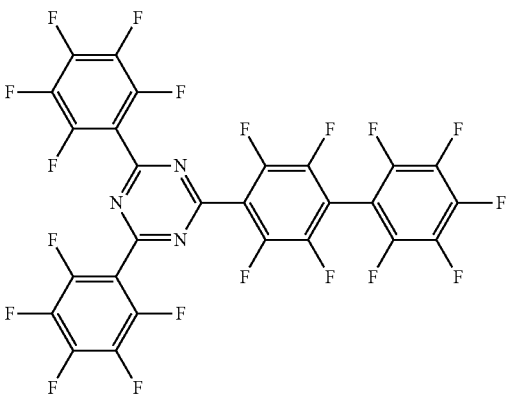
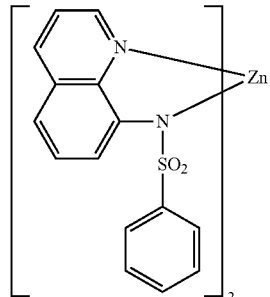
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		Appl. Phys. Lett. 55, 1489 (1989)
		Jpn. J. Apply. Phys. 32, L917 (1993)
Silole compounds		Org. Electron. 4, 113 (2003)
Arylborane compounds		J. Am. Chem. Soc. 120, 9714 (1998)
Fluorinated aromatic compounds		J. Am. Chem. Soc. 122, 1832 (2000)
Fullerene (e.g., C60)		U.S. 20090101870

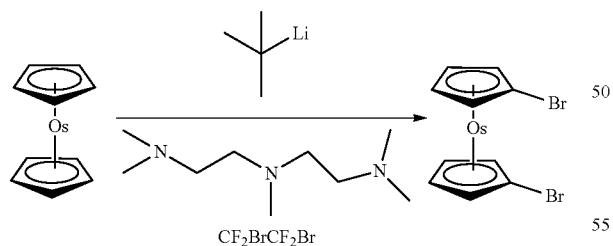
TABLE A-continued

MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Triazine complexes		U.S. 20040036077
Zn (N N) complexes		U.S. Pat. No. 6,528,187

## EXPERIMENTAL

## Synthesis of Exemplary Compounds of the Invention

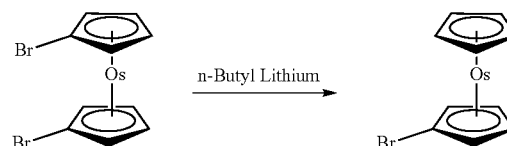
Synthesis of Compound 1  
 Synthesis of 1,1' Dibromoosmocene



Osmocene (0.47 g, 1.467 mmol) was placed in a 100 mL round-bottomed flask, and then N1-(2-(dimethylamino) ethyl)-N1,N2,N2-trimethylethane-1,2-diamine (0.919 ml, 4.40 mmol) and pentane (30 ml) were added and stirred to give a white suspension. Tert-butyllithium (2.59 ml, 4.40 mmol) was added at 0° C., the reaction mixture was subjected to sonication for 1 h, and then it was stirred at room temperature for 5.5 h. 1,2-dibromo-1,1,2,2-tetrafluoroethane (1.049 ml, 8.80 mmol) was added dropwise at -78° C. The dry ice bath was removed and the reaction mixture was

stirred overnight. The reaction mixture was diluted with water and extracted by dichloromethane. The organic portion was subjected to column chromatography (SiO<sub>2</sub>, 30% DCM in heptane) to yield the desired product (0.525 g, 75%).

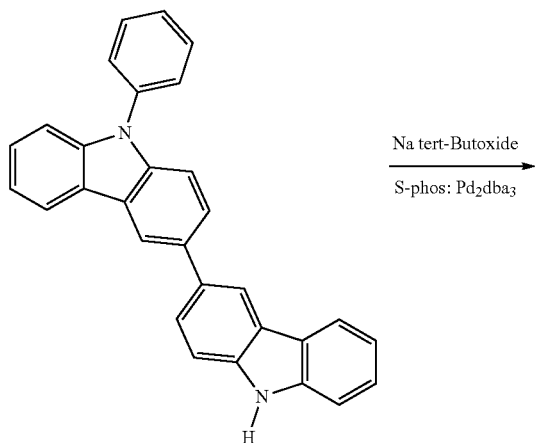
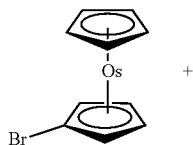
## Synthesis of Bromoosmocene



A 100 mL round-bottomed flask was charged with 1,1' dibromoosmocene (0.462 g, 0.966 mmol) and THF (Volume: 20 ml) to give a colorless solution. N-butyllithium (0.425 ml, 1.063 mmol) was added at -78° C., and the reaction temperature was maintained below -60° C. for 1 h. The reaction mixture was then quenched with saturated aqueous ammonium chloride solution. The reaction mixture was extracted with dichloromethane. The organic portion was concentrated to yield the desired product (0.316 g, 82%).

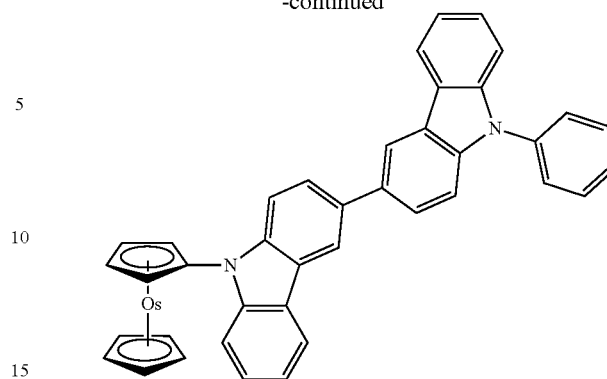
## 139

Synthesis of Compound 1



## 140

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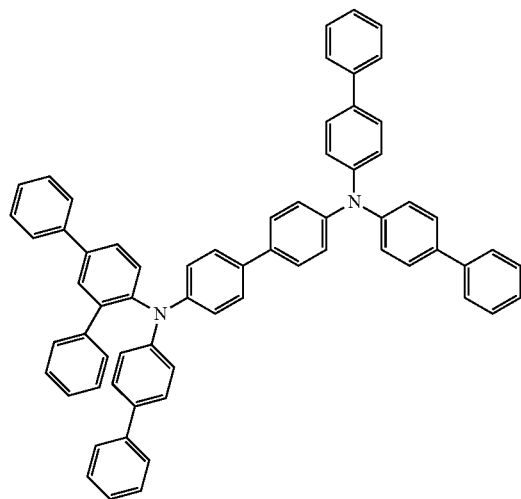


Compound 1

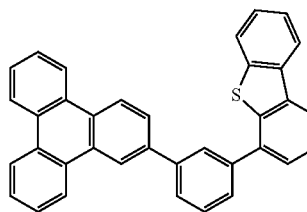
One 500 mL round-bottomed flask was charged with bromoosmocene (3.24 g, 8.11 mmole), 9-phenyl-9H,9'H-3, 3'-bicarbazole (3.48 g, 8.52 mmol), Pd<sub>2</sub>dba<sub>3</sub> (0.149 g, 0.162 mmole), dicyclohexyl(2',6'-dimethoxy-[1,1'-biphenyl]-3-yl) phosphane (0.266 g, 0.649 mmol), sodium t-butoxide (1.950 g, 24.34 mmol) and Xylene (200 ml) to give a brown suspension. The reaction mixture was refluxed for 19 h. The reaction mixture was then diluted with water and extracted with ethyl acetate. The organic portion was then combined and subjected to column chromatography (Al<sub>2</sub>O<sub>3</sub>, basic, toluene:heptane=1:9 to 5:5) to yield 4.5 g of Compound 1 (76%).

## Device Examples

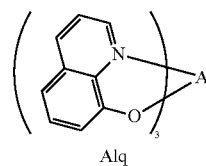
## Materials Used in the Devices



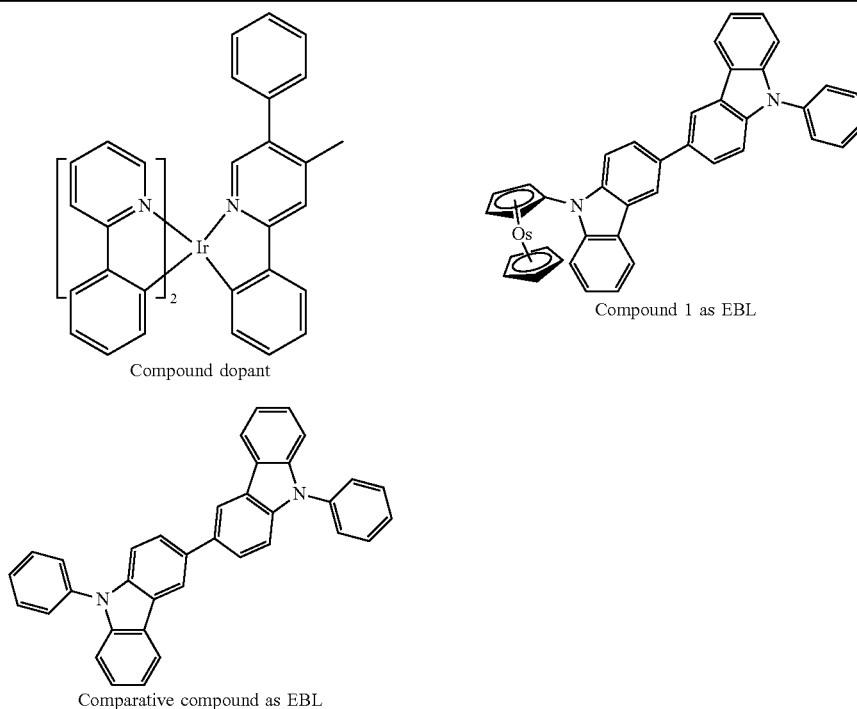
Compound HTL



Compound Host



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**Device Structure:**

All example devices were fabricated by high vacuum ( $<10^{-7}$  Torr) thermal evaporation. The anode electrode is 1200 Å of indium tin oxide (ITO). The cathode consisted of 10 Å of LiF followed by 1,000 Å of Al. All devices were encapsulated with a glass lid sealed with an epoxy resin in a nitrogen glove box ( $<1$  ppm of  $H_2O$  and  $O_2$ ) immediately after fabrication, and a moisture getter was incorporated inside the package. The organic stack of the device examples consisted of sequentially, from the ITO surface, 100 Å of LG-101 (available from LG Chem. Inc.) as the hole injection layer (HIL), 400 Å of Compound HTL as the hole transporting layer (HTL), 50 Å of Compound 1 or comparative compound as the electron blocking layer (EBL), 300 Å of a compound host doped with 12 wt % of compound dopant as the emissive layer (EML), 50 Å of Compound Host as a blocking layer (BL), 400 Å of Alq (tris-8-hydroxyquinoline aluminum) as the ETL. The device results and data are summarized in Table 1.

the device to decay to 80% of its initial luminance under a constant current density of 40 mA/cm<sup>2</sup>. The difference between the structure of Compound 1 and the comparative compound, is that Compound 1 has the osmocene moiety while the comparative compound does not have it. The device lifetime data clearly indicate that when Compound 1 is used as an EBL material, it is about 1.5 fold more stable than the comparative compound. This is attributable to the high hole injection ability of osmocene, which helps to balance charge fluxes. The balanced electron/hole fluxes spread the charge recombination zone, which preserves a high efficiency at high brightness by suppressing or reducing exciton quenching. An expanded charge recombination zone also extends the device lifetime by allowing a larger population of molecules to have charge transport, exciton formation, and light emission roles.

It is understood that the various embodiments described herein are by way of example only, and are not intended to limit the scope of the invention. For example, many of the

TABLE 1

		At 1000 nits						At 40 mA/cm2 LT
Example	EBL	1931 CIE		λ max	LE	EQE	PE	80% LT
		x	y	[nm]	[cd/A]	[%]	[lm/W]	[h]
Device Example	Compound 1	0.325	0.629	526	67.8	18.7	42.7	296
Comparative	Comparative	0.325	0.629	525	68.6	18.9	43.0	193
Device Example	compound							

Table 1 is a summary of the device data. The luminous efficiency (LE), external quantum efficiency (EQE), and power efficiency (PE) were measured at 1000 units, while the lifetime (LT80%) was defined as the time required for

materials and structures described herein may be substituted with other materials and structures without deviating from the spirit of the invention. The present invention as claimed may therefore include variations from the particular

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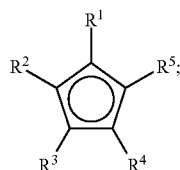
examples and preferred embodiments described herein, as will be apparent to one of skill in the art. It is understood that various theories as to why the invention works are not intended to be limiting.

The disclosures of each and every patent, patent application, and publication cited herein are hereby incorporated herein by reference in their entirety. While this invention has been disclosed with reference to specific embodiments, it is apparent that other embodiments and variations of this invention may be devised by others skilled in the art without departing from the true spirit and scope of the invention. The appended claims are intended to be construed to include all such embodiments and equivalent variations.

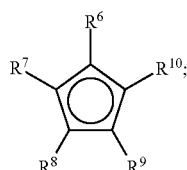
I claim:

1. A compound having an osmocene structure having a formula of  $\text{Os}(\text{L}^1)(\text{L}^2)$ :

wherein  $\text{L}^1$  has the formula:



wherein  $\text{L}^2$  has the formula:



wherein  $\text{R}^1$  to  $\text{R}^{10}$  are each independently selected from the group consisting of hydrogen, deuterium, halogen, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, heterocyclyl, acyl, carbonyl, carboxylic acid, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof; and

wherein at least one of  $\text{R}^1$  to  $\text{R}^{10}$  comprises at least one chemical group selected from the group consisting of triphenylene, carbazole, dibenzothiophene, dibenzofuran, dibenzoselenophene, azatriphenylene, azacarbazole, aza-dibenzothiophene, aza-dibenzofuran, and aza-dibenzoselenophene.

2. The compound of claim 1, wherein at least one of  $\text{R}^1$  to  $\text{R}^{10}$  comprises at least one chemical group selected from the group consisting of biphenyl, triphenyl, triphenylene, naphthalene, anthracene, phenalene, phenanthrene, fluorene, pyrene, chrysene, perylene, and azulene.

3. The compound of claim 1, wherein at least one of  $\text{R}^1$  to  $\text{R}^{10}$  comprises at least one chemical group selected from the group consisting of dibenzothiophene, dibenzofuran, dibenzoselenophene, furan, thiophene, benzofuran, benzothiophene, benzoselenophene, carbazole, indolocarbazole, pyridylindole, pyrrolodipyridine, pyrazole, imidazole, triazole, oxazole, thiazole, oxadiazole, oxatriazole, dioxazole, thiadiazole, pyridine, pyridazine, pyrimidine, pyrazine, triazine, oxazine, oxathiazine, oxadiazine, benzimidazole, indazole, indoxazine, benzoxazole, benzisoxazole, benzothiazole, quinoline, isoquinoline, cinnoline, quinazoline, quinoxaline, naphthyridine, phthalazine, pteridine, xan-

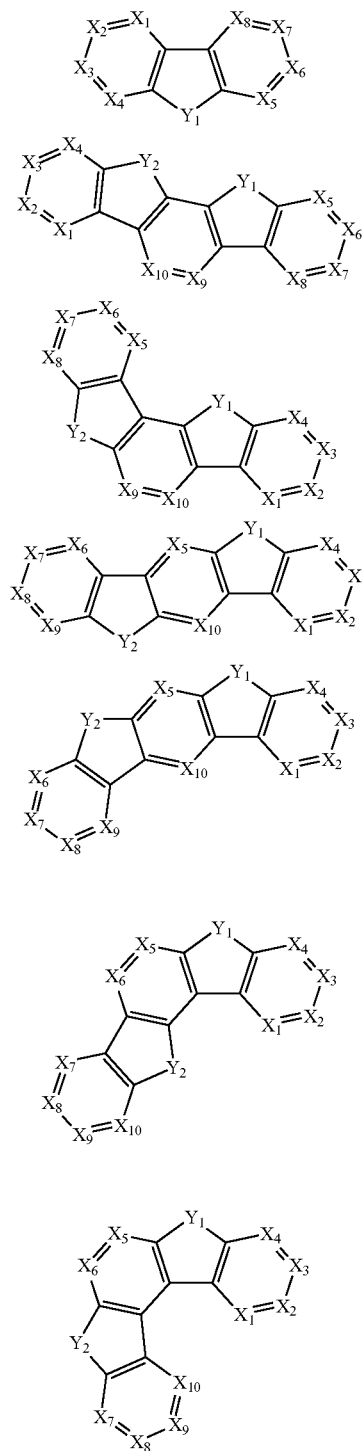
## 144

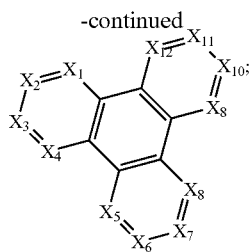
thene, acridine, phenazine, phenothiazine, phenoxazine, benzofuopyridine, furodipyridine, benzothienopyridine, thienodipyridine, benzoselenophenopyridine, selenophenodipyridine, aza analogs thereof, and combinations thereof.

4. The compound of claim 1, wherein at least one of  $\text{R}^1$  to  $\text{R}^{10}$  is L-G;

wherein L is a direct bond or an organic linker; and

wherein G is selected from the group consisting of:

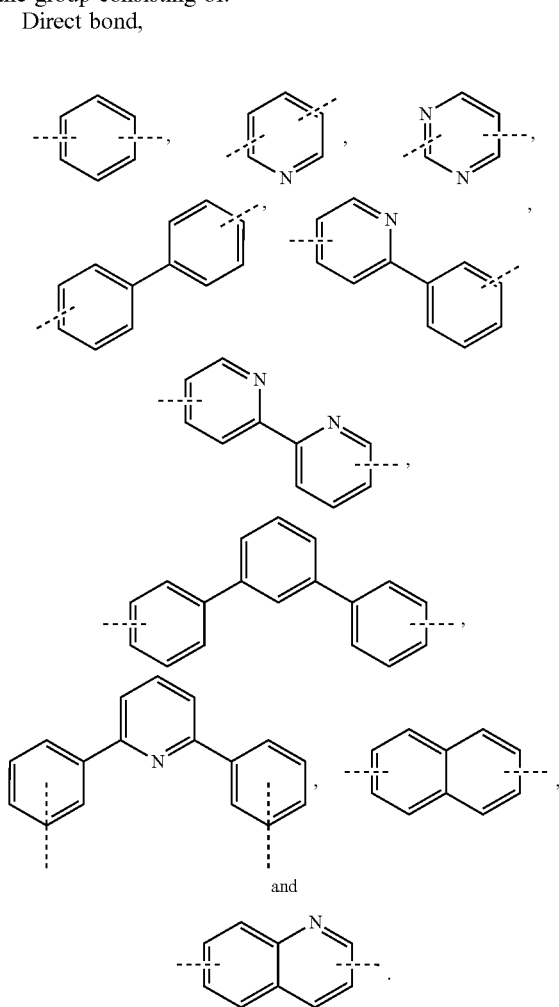


**145**

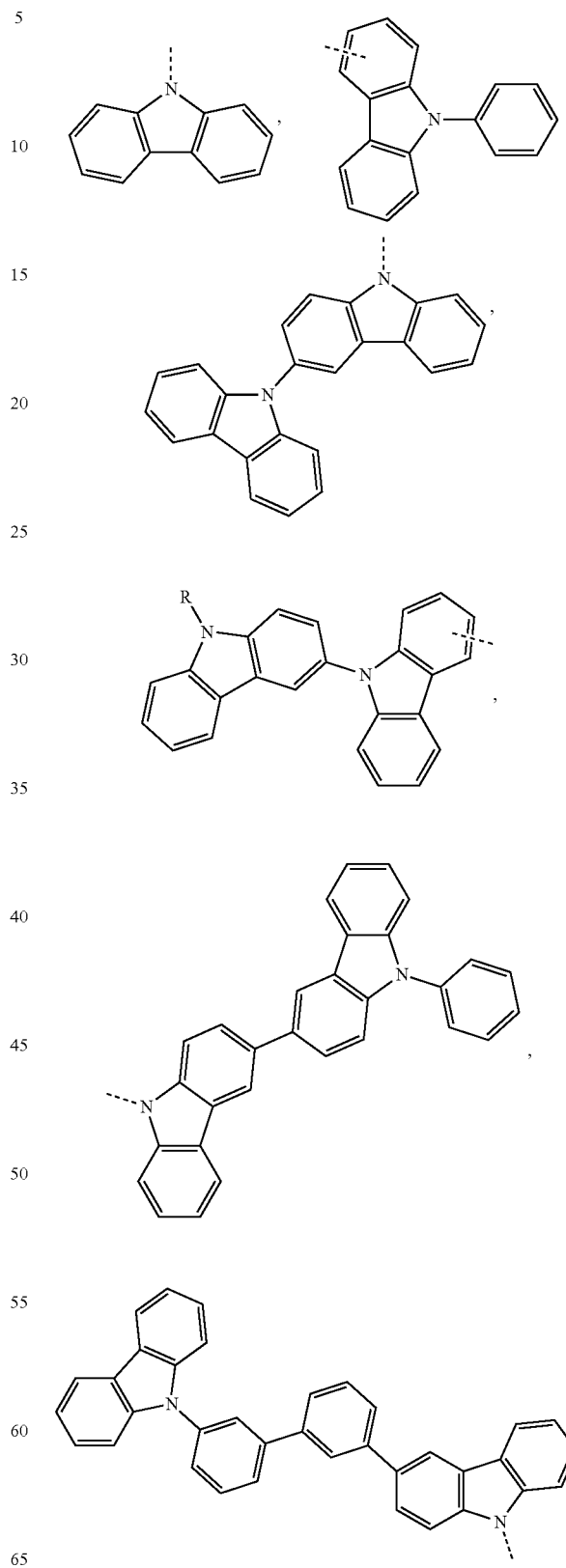
wherein  $Y_1$  and  $Y_2$  are independently selected from the group consisting of  $NR^{11}$ ,  $CR^{11}R^{12}$ , O, S, and Se; wherein  $X_1$  to  $X_{12}$  are independently selected from the group consisting of  $CR^{13}$  and N, and wherein  $R^{11}$ ,  $R^{12}$ , and  $R^{13}$  are each independently selected from the group consisting of hydrogen, deuterium, halogen, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, heteroaryl, acyl, carbonyl, carboxylic acid, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof; and wherein any two adjacent substituents of  $R^{11}$ ,  $R^{12}$ , and  $R^{13}$  are optionally fused or joined to form a ring.

5. The compound of claim 1, wherein at least one of  $R^1$  to  $R^{10}$  comprises at least one carbazole group.

6. The compound of claim 4, wherein L is selected from the group consisting of:

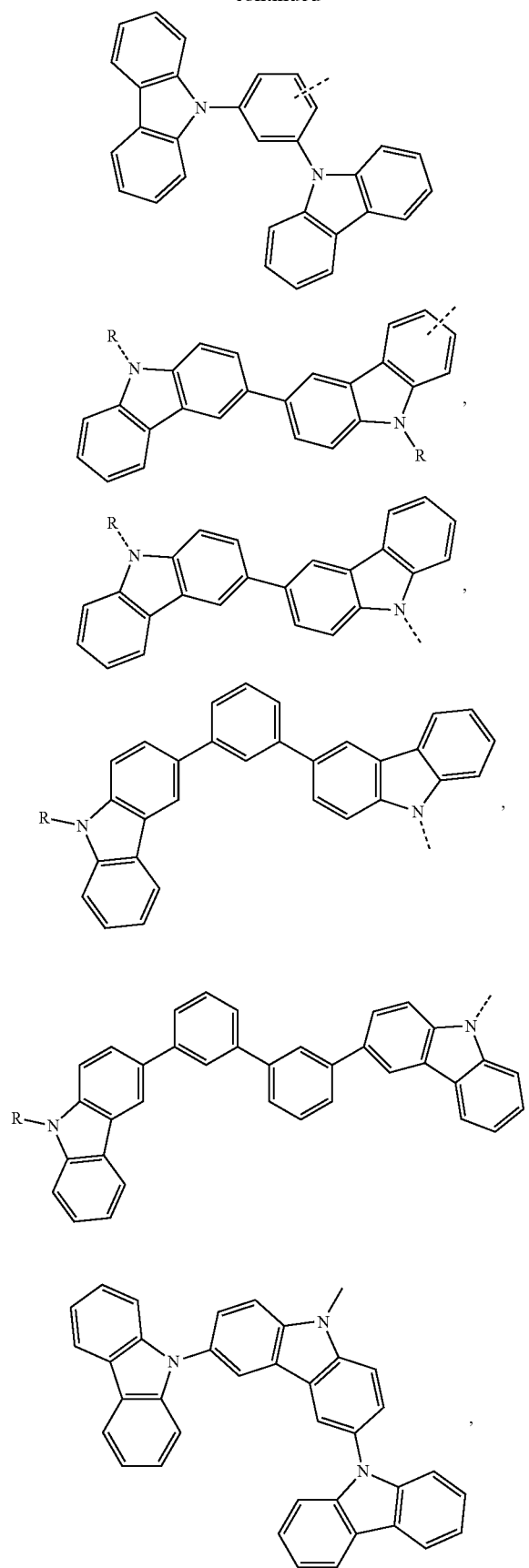
**146**

7. The compound of claim 4, wherein G is selected from the group consisting of:

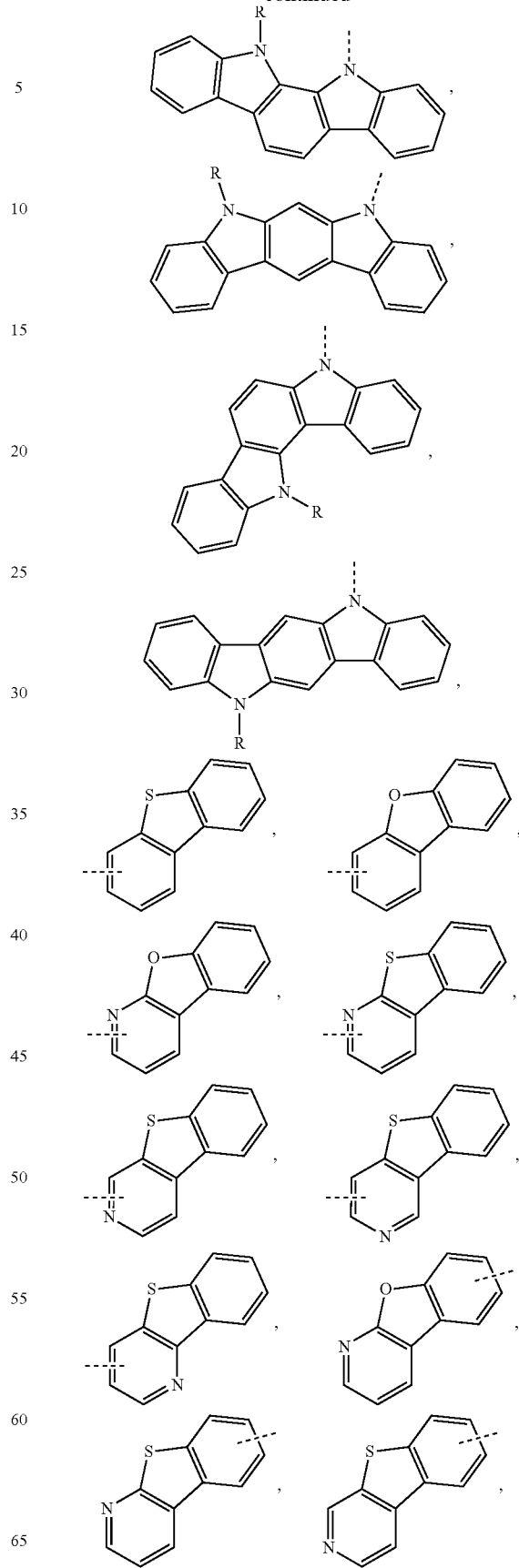


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**148**

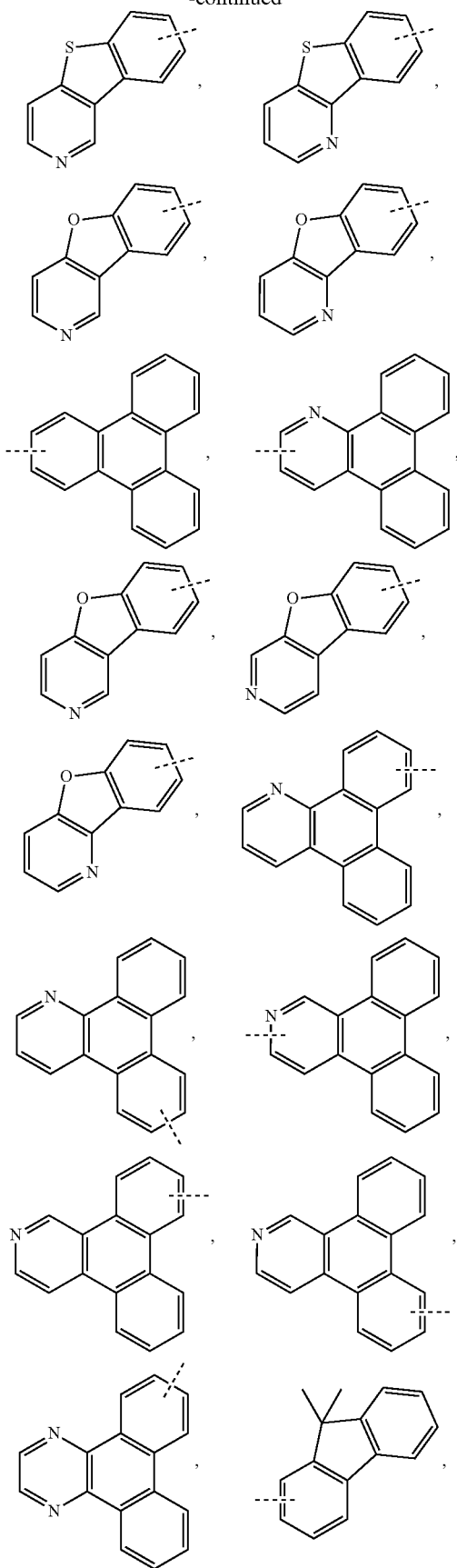
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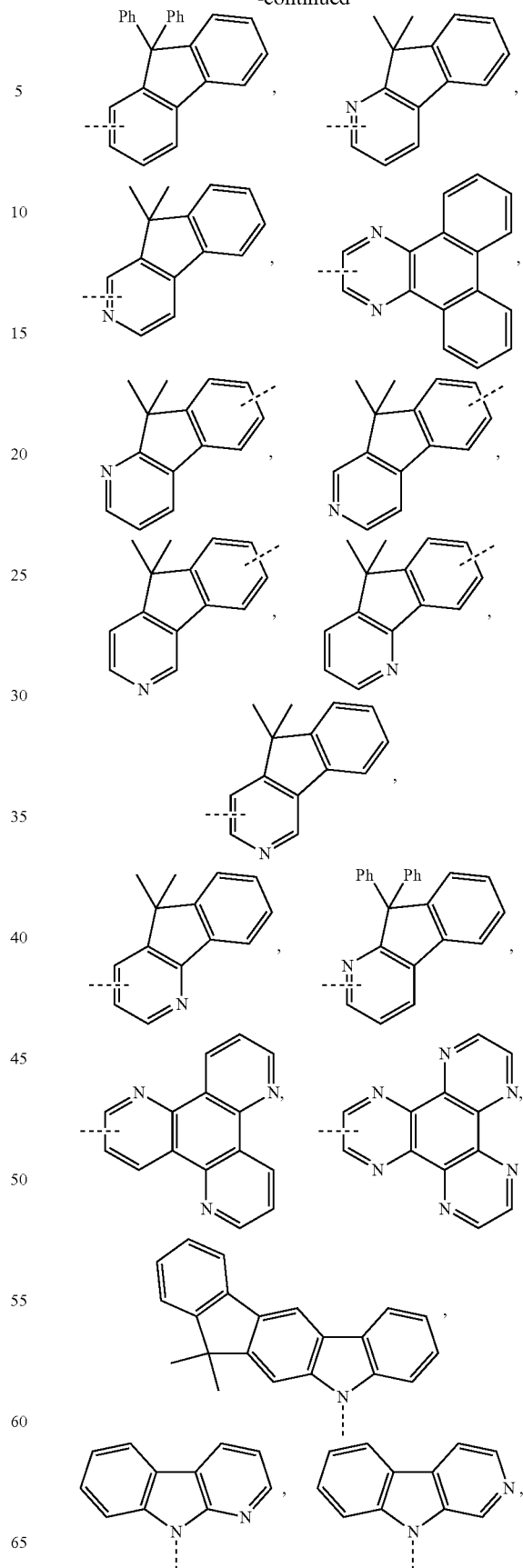
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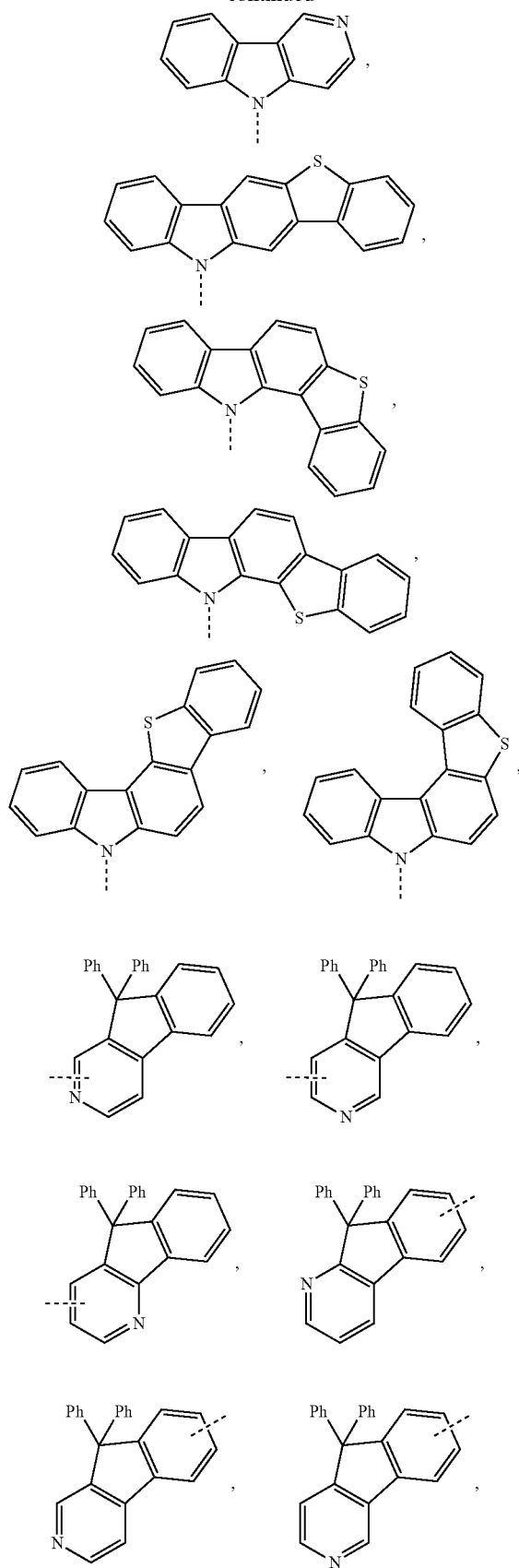
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**151**

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**152**-continued  
and

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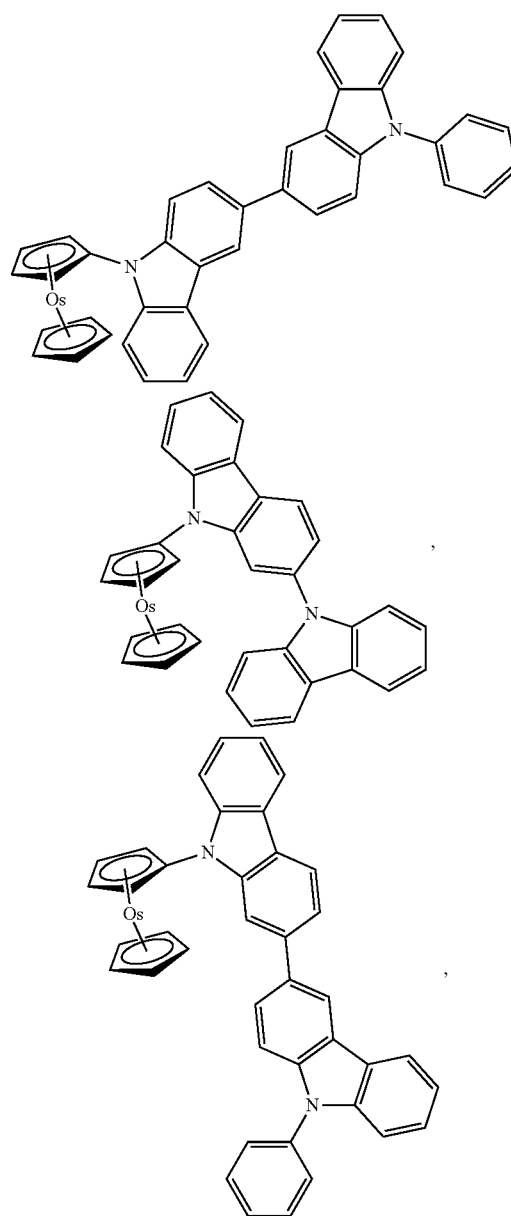
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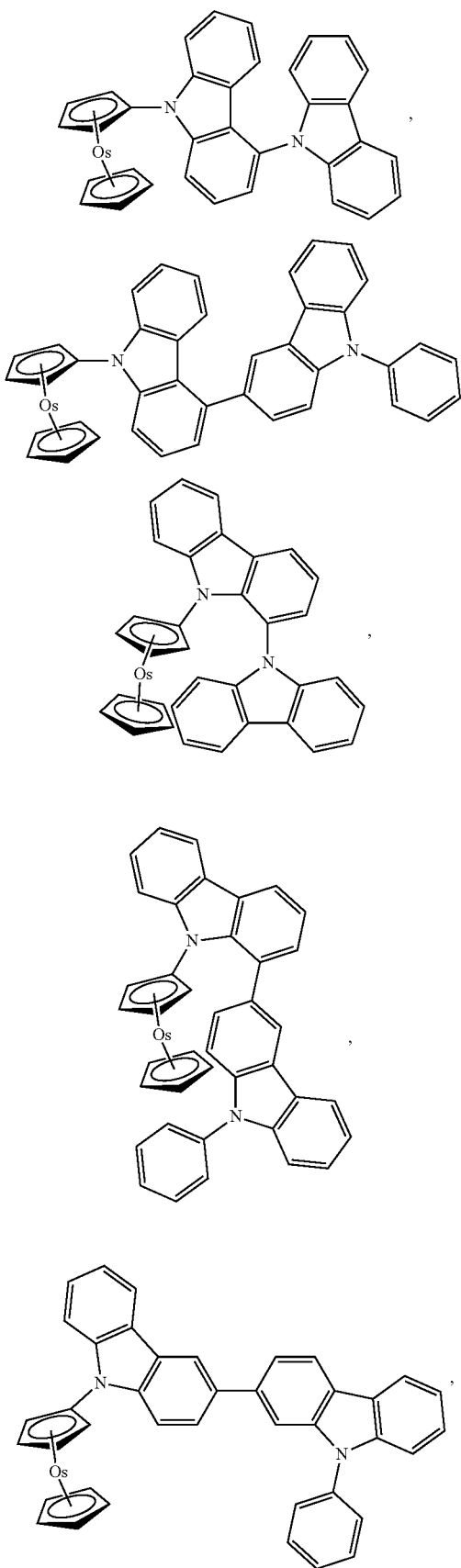
wherein R is selected from the group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryl, heteroaryl, aryloxy, amino, and combinations thereof.

8. The compound of claim 1, wherein the compound is selected from the group consisting of:

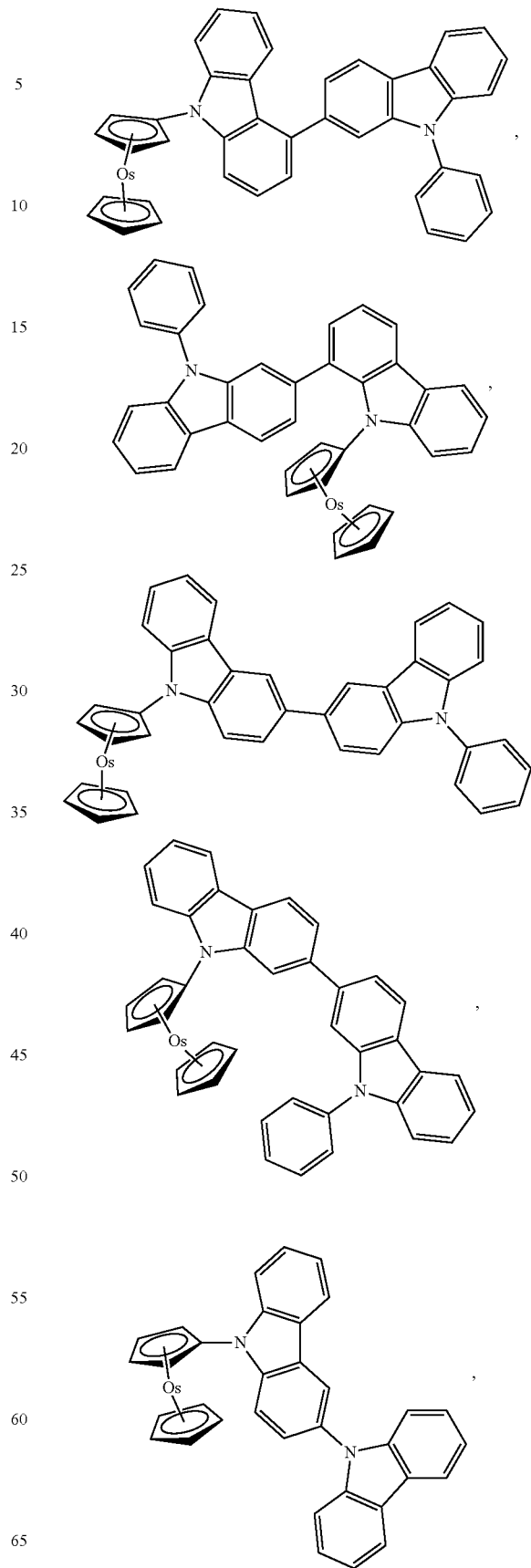


**153**

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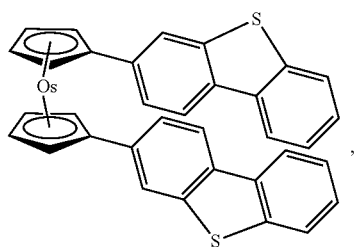
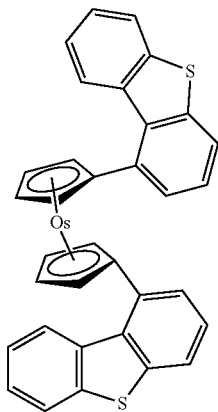
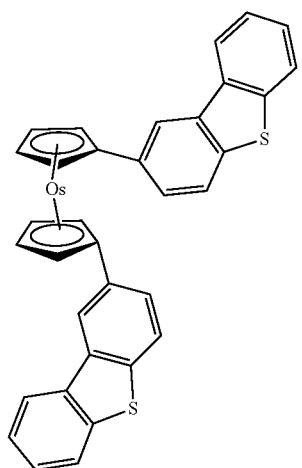
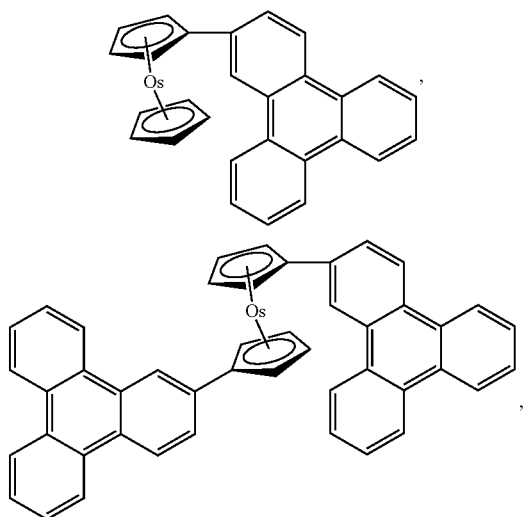
**154**

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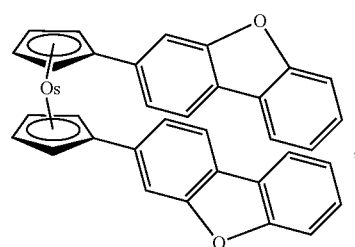
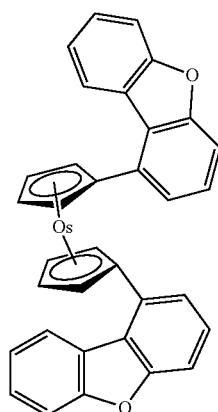
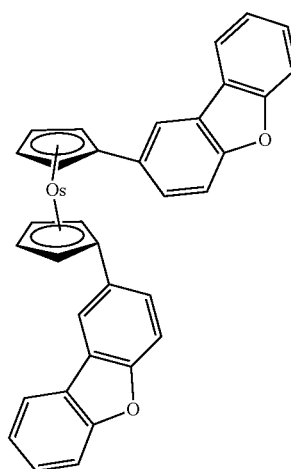
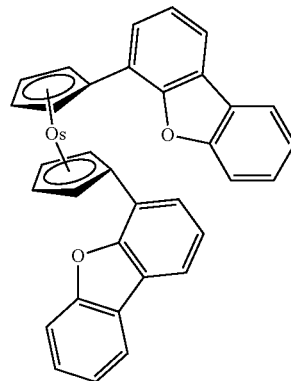


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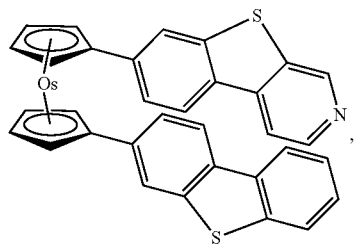
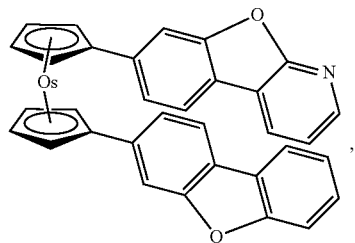
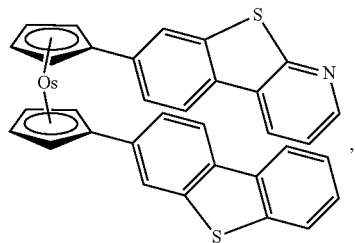
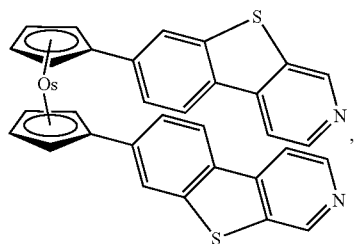
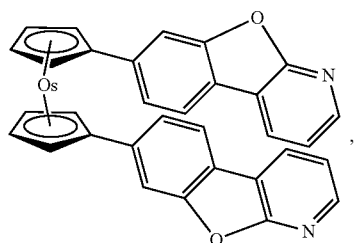
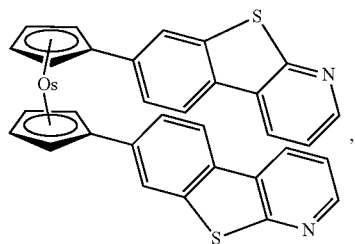
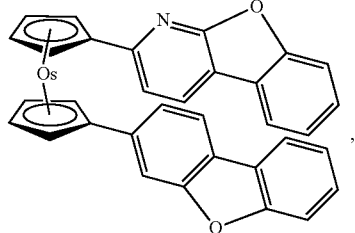
**156**

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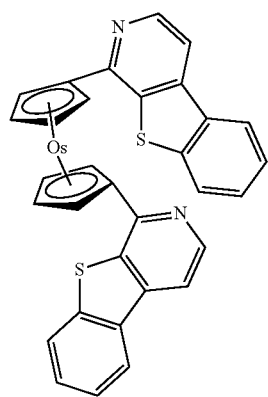
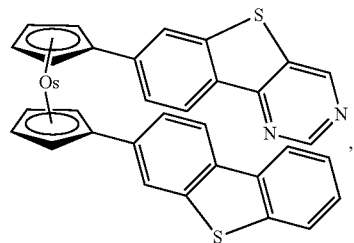
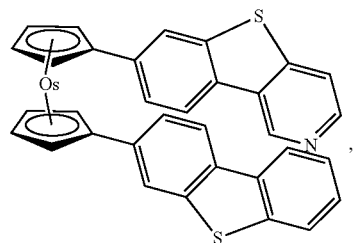
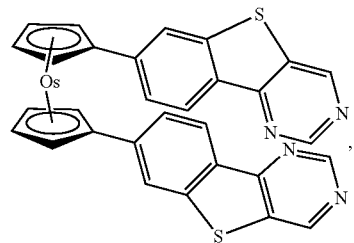
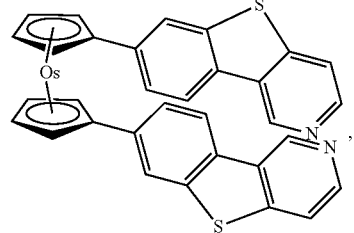


**157**

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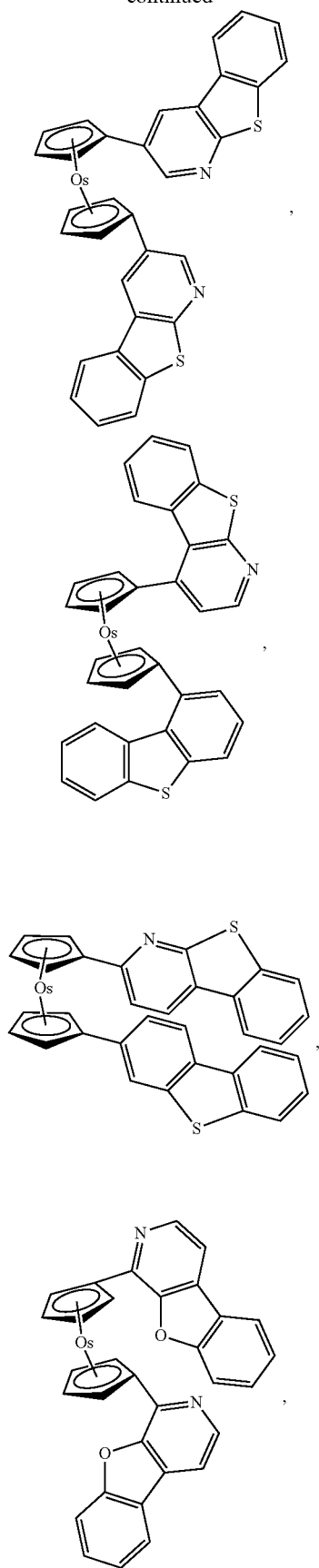
**158**

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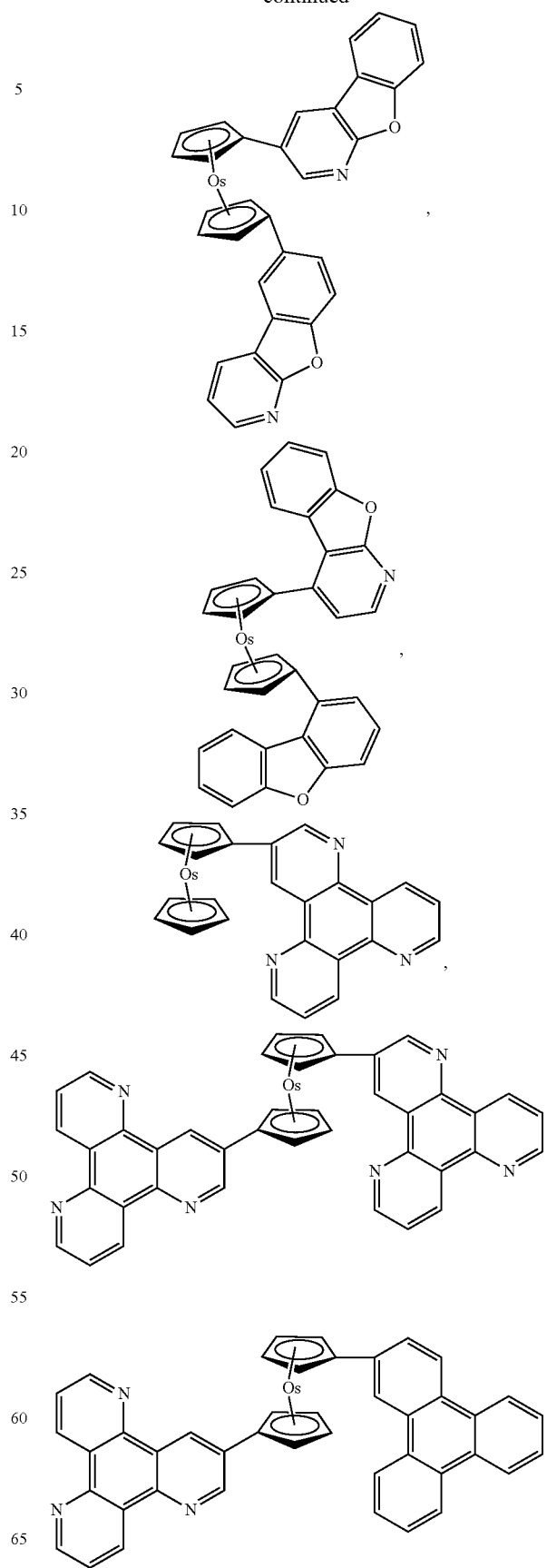


**159**

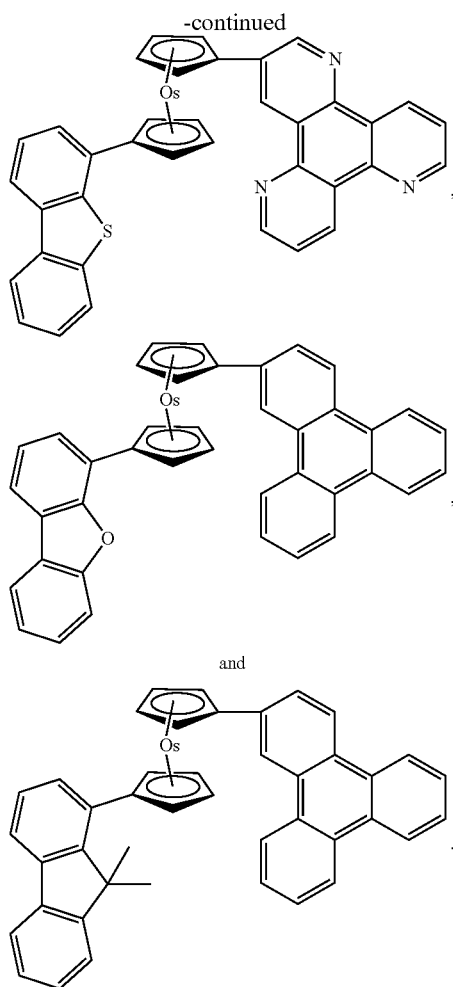
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**160**

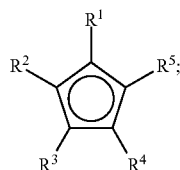
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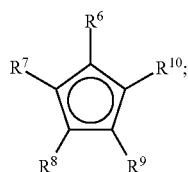
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9. A first device comprising a first organic light emitting device, the first organic light emitting device comprising:  
 an anode;  
 a cathode; and  
 an organic layer, disposed between the anode and the cathode, comprising a compound having an osmium structure having a formula of  $\text{Os}(\text{L}^1)(\text{L}^2)$ ;  
 wherein  $\text{L}^1$  has the formula:



wherein  $\text{L}^2$  has the formula:



wherein  $\text{R}^1$  to  $\text{R}^{10}$  are each independently selected from the group consisting of hydrogen, deuterium, halogen,

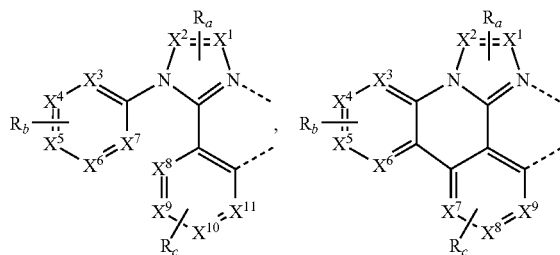
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alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, heterocyclyl, acyl, carbonyl, carboxylic acid, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof; and

wherein at least one of  $\text{R}^1$  to  $\text{R}^{10}$  comprises at least one chemical group selected from the group consisting of triphenylene, carbazole, dibenzothiophene, dibenzofuran, dibenzoselenophene, azatriphenylene, azacarbazole, aza-dibenzothiophene, aza-dibenzofuran, and aza-dibenzoselenophene.

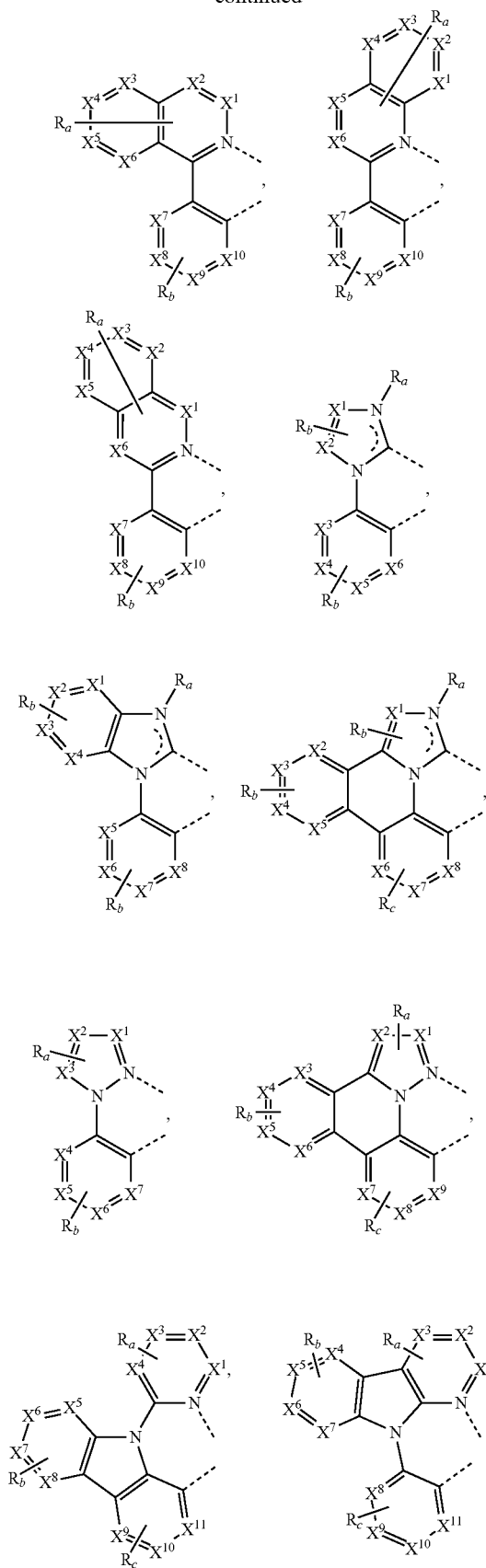
10. The first device of claim 9, wherein the organic layer is an emissive layer and the compound is a host.

11. The first device of claim 9, wherein the organic layer further comprises a phosphorescent emissive dopant; wherein the emissive dopant is a transition metal complex having at least one ligand or part of the ligand if the ligand is more than bidentate selected from the group consisting of:



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and

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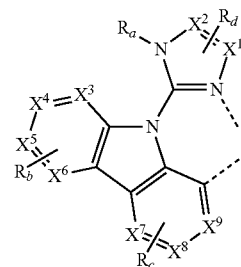
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wherein each X<sup>1</sup> to X<sup>13</sup> are independently selected from the group consisting of carbon and nitrogen;

wherein X is selected from the group consisting of BR', NR', PR', O, S, Se, C=O, S=O, SO<sub>2</sub>, CR'R'', SiR'R'', and GeR'R'';

wherein R' and R'' are optionally fused or joined to form a ring;

wherein each R<sub>a</sub>, R<sub>b</sub>, R<sub>c</sub>, and R<sub>d</sub> may represent from mono substitution to the possible maximum number of substitution, or no substitution;

wherein R', R'', R<sub>a</sub>, R<sub>b</sub>, R<sub>c</sub>, and R<sub>d</sub> are each independently selected from the group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acids, ester, nitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof; and

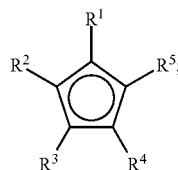
wherein any two adjacent substituents of R<sub>a</sub>, R<sub>b</sub>, R<sub>c</sub>, and R<sub>d</sub> are optionally fused or joined to form a ring or form a multidentate ligand.

12. The first device of claim 9, wherein the organic layer is an electron blocking layer and the compound is an electron blocking material in the organic layer.

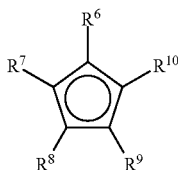
13. The first device of claim 9, wherein the organic layer is a transporting layer and the compound is a transporting material in the organic layer.

14. The first device of claim 9, wherein the device is selected from the group consisting of a consumer product, an electronic component module, an organic light-emitting device, and a lighting panel.

15. A formulation comprising a compound having an osmocene structure having a formula of Os(L<sup>1</sup>)(L<sup>2</sup>); wherein L<sup>1</sup> has the formula:



wherein L<sup>2</sup> has the formula:





wherein  $R^1$  to  $R^{10}$  are each independently selected from the group consisting of hydrogen, deuterium, halogen, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, heterocyclyl, acyl, carbonyl, carboxylic acid, 5 ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof; and wherein at least one of  $R^1$  to  $R^{10}$  comprises at least one chemical group selected from the group consisting of triphenylene, carbazole, dibenzothiophene, dibenzofuran, diben- 10 zoselenophene, azatriphenylene, azacarbazole, aza-dibenzothiophene, aza-dibenzofuran, and aza-dibenzoselenophene.

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